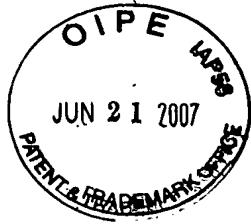


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DECLARATION

I, Mari Kawanishi, a staff member of TAIYO, NAKAJIMA & KATO, Eighth Floor, 3-17, Shinjuku 4-chome, Shinjuku-ku, Tokyo 160-0022, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the documents in respect of Japanese Patent Application No. 2003-058549, that was filed on 5th March, 2003 in the name of FUJI PHOTO FILM CO., LTD.

Dated this 19th day of June, 2007

Mari Kawanishi

Mari Kawanishi

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[TITLE OF THE INVENTION]

IMAGE FORMING METHOD

[Claims]

[Claim 1] An image forming method for forming an image with an image recording apparatus including laser irradiation means for scan exposing, with a laser beam, a photothermographic material comprising a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder on at least one surface of a support, and means for transporting the photothermographic material in a sub scanning direction and guiding it to a thermal developing portion, wherein:

- 1) the photothermographic material comprises at least one compound selected from compounds represented by the following formulae (1a), (1b) and (1c); and
- 2) a distance between a scanning line of the laser irradiation means and an insertion part of the thermal developing portion is 50 cm or less;

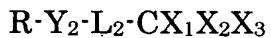
Formula (1a)



wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom; L_1 represents a sulfonyl group; $n1$ represents 0 or 1; Y_1 represents $-N(R_1)-$, a sulfur atom, an oxygen atom, a selenium atom, or $-(R_2)C=C(R_3)-$; R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a

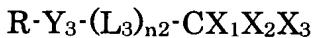
heterocyclic group;

Formula (1b)



wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom; L_2 represents a carbonyl group or a sulfinyl group; Y_2 represents $\cdot N(R_1)\cdot$, a sulfur atom, an oxygen atom, a selenium atom, or $\cdot (R_2)C=C(R_3)\cdot$; R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a heterocyclic group; and

Formula (1c)



wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom; L_3 represents a sulfonyl group, a carbonyl group or a sulfinyl group; $n2$ represents 2 or 3; Y_3 represents a single bond, $\cdot N(R_1)\cdot$, a sulfur atom, an oxygen atom, a selenium atom, or $\cdot (R_2)C=C(R_3)\cdot$; R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a heterocyclic group.

[Claim 2] An image forming method according to claim 1, wherein, in Formulae (1a), (1b) and (1c), R is an alkyl group.

[Claim 3] An image forming method according to claim 1 or 2, wherein, in Formulae (1a), (1b) and (1c), at least one of X_1 , X_2 and X_3 is Br .

[Claim 4] An image forming method according to any of claims 1 to 3, wherein, in Formula (1a), Y_1 is $-N(R_1)-$.

[Claim 5] An image forming method according to claim 4, wherein, in Formula (1a), R_1 is an alkyl group.

[Claim 6] An image forming method according to any of claims 1 to 3, wherein, in Formula (1b), Y_2 is $-N(R_1)-$.

[Claim 7] An image forming method according to claim 6, wherein, in Formula (1b), R_1 is a hydrogen atom.

[Claim 8] An image forming method according to any of claims 1 to 3, wherein, in Formula (1c), Y_3 is a single bond.

[Claim 9] An image forming method according to any of claims 1 to 3, and 8, wherein, in Formula (1c), n_2 represents 2.

[Claim 10] An image forming method according to any of claims 1 to 9, wherein, in Formulae (1a), (1b) and (1c), R and R_1 , or R and R_3 form a ring.

[Claim 11] An image forming method according to claim 10, wherein the ring is an alicyclic group.

[Claim 12] An image forming method according to any of claims 1 to 11, wherein the distance between the scanning line and the insertion part of the thermal developing portion is 45 cm or less.

[Claim 13] An image forming method according to any of claims 1 to 12, wherein the photothermographic material has a silver coating amount of 1.9 g or less per 1 m² of the photothermographic material.

[Claim 14] An image forming method according to any of claims 1 to 13, wherein thermal development is carried out for 6 seconds to 14 seconds.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to an image forming method utilizing thermal development.

[0002]

[Prior Art]

In recent years, it has been strongly desired in the field of films for medical imaging to reduce the amount of used processing liquid waste in consideration of environmental protection and space saving. For this reason, technology for photothermographic materials for medical imaging and for photographic applications, which are capable of efficient exposure with a laser image setter or a laser imager and capable of forming a clear black-toned image

with high resolution and high sharpness is desired. Such photothermographic materials can eliminate use of solution-based processing chemicals and can provide users with a thermal development system which is simpler and does not contaminate the environment.

[0003]

Although similar requirements also exist in the field of general image forming materials, an image for medical imaging requires a particularly high image quality excellent in sharpness and granularity because a delicate image presentation is necessitated. Also an image of blue-black tone is preferred in consideration of easy diagnosis. Currently various hard copy systems utilizing pigments or dyes, such as ink jet printers and electrophotographic systems, are available as general image forming systems, but they are not satisfactory as output systems for medical images.

[0004]

On the other hand, thermal image forming systems utilizing organic silver salts are known (see, for example, Patent Documents 1 and 2, and Non-Patent Document 1). More specifically, a photothermographic material generally comprises a photosensitive layer in which a catalytically active amount of photocatalyst (for example, a silver halide), a reducing agent, a reducible silver salt (for example, an organic silver salt) and, if necessary, a toner for controlling the tone of a developed silver image are dispersed in a matrix of a binder. The photothermographic material, when heated at high temperature (for example, 80°C or higher) after image exposure, forms a black-toned silver image by an

oxidation/reduction reaction between the reducible silver salt (functioning as an oxidizer) and the reducing agent. The oxidation/reduction reaction is promoted by a catalytic effect of a latent image of silver halide formed by exposure.

Accordingly, a black-toned silver image is formed in an exposed area (see, for example, Patent Documents 3 and 4). Further, Fuji Medical Dry Laser Imager FM-DP L has been marketed as a practical medical image forming system using a photothermographic material (see, for example, Non-Patent Document 2).

[0005]

A photothermographic material comprising a photosensitive silver halide and a non-photosensitive organic salt has a high sensitivity and is extremely suitable as an image recording material for the aforementioned laser output, and applications in such fields are anticipated to further increase in the future. For such expansion of the applications and for an increase in processing amount, further improvement in an image recording speed and a developing speed, improved adaptability to an installation location of the apparatus and its environment, and downsizing of the entire apparatus including an optical system for laser exposure and a thermal developing portion are required.

[0006]

An advanced image recording apparatus integrating a laser exposing portion and a thermal developing portion and not requiring water supplying and discharging pipes and an exhaust pipe for a discharged gas has been developed and widely utilized (see, for example, Patent Documents 1 and 2, and Non-Patent Document 1). In such apparatuses, a photothermographic material is at first

transported to a laser exposing portion, then, after image data is written by scanning exposure, it is guided to a thermal developing portion and heated to form an image. Thereafter it is cooled and discharged from the apparatus. However in such apparatus, since the laser exposing portion and the thermal developing portion are sufficiently separated to avoid mutual detrimental influence, the entire apparatus lacks compactness and requires a large space for installation.

[0007]

One way for downsizing the total system is to position the laser exposing portion and the thermal developing portion closer to each other. Conventionally, the thermal developing portion has been equipped with a heat source for uniform heating at about 120°C, and is formed with a material having an increased heat capacity at a high temperature in order to moderate a temperature variation. Also, in order to avoid heat leakage, it is entirely covered with a heat insulating material. However, in order to avoid a temperature increase in the laser exposing portion due to heat conduction by a recording material or due to heat diffusion by leaking air, the thermal developing portion and the laser exposing portion have been designed to have a sufficient distance therebetween. The conventional object of preventing a temperature increase of the laser exposing portion has principally been to maintain precision in an optical system.

[0008]

In a photothermographic material, a staining in the optical system due to volatile substances generated by heating is another specific factor in addition to

deviation in the precision of the optical system due to heat. This problem can be alleviated by designing a photothermographic material showing reduced generation of volatile substances under heating, but another problem has been newly discovered. In the case of executing exposure and thermal development of the photothermographic material in a continuous manner in an apparatus in which a laser exposing portion and a thermal developing portion are positioned close to each other, the sensitivity of a first photothermographic material and that of a subsequent (for example a 20th) photothermographic material are clearly different. Such change is assumed to be generated gradually and continuously, and the difference only becomes clearly recognizable between the first material and approximately the 20th material.

[0009]

Since a system is required to always have a constant sensitivity, this is an important issue in reducing the size of the apparatus. Although its cause is not yet clear and such a problem may be caused by a local or partial temperature variation and deviation in the apparatus during continuous development, a photothermographic material that is not affected by such variation is desired.

[0010]

[Patent Document 1]

U.S. Patent No. 3152904

[Patent Document 2]

U.S. Patent No. 3457075

[Patent Document 3]

U.S. Patent No. 2910377

[Patent Document 4]

Japanese Patent Application Publication (JP·B) No. 43-4924

[Non-Patent Document 1]

"Thermally Processed Silver Systems", written by D. H. Klosterboer, appearing in "Imaging Processes and Materials", Neblette, 8th edition, edited by J. Sturge, V. Walworth, and A. Shepp, Chapter 9, page 279, 1989

[Non-Patent Document 2]

Fuji-Medical Review No.8, pages 39 to 55 (1999)

[0011]

[Problems to be Solved by the Invention]

Thus, an object of the present invention is to provide an image forming method capable of outputting an image with stable sensitivity, utilizing a compact apparatus for laser exposure and thermal development in which a laser exposing portion and a thermal developing portion are positioned close to each other.

[0012]

[Means for Solving the Problems]

The objects of the invention have been accomplished by the following image forming method.

<1> An image forming method for forming an image with an image recording apparatus including laser irradiation means for scan exposing, with a laser beam, a photothermographic material comprising a photosensitive silver halide, a non-

photosensitive organic silver salt, a reducing agent and a binder on at least one surface of a support, and means for transporting the photothermographic material in a sub scanning direction and guiding it to a thermal developing portion, wherein:

- 1) the photothermographic material comprises at least one compound selected from compounds represented by the following formulae (1a), (1b) and (1c); and
- 2) a distance between a scanning line of the laser irradiation means and an insertion part of the thermal developing portion is 50 cm or less;

[0013]

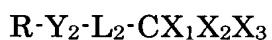
Formula (1a)



wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom; L_1 represents a sulfonyl group; $n1$ represents 0 or 1; Y_1 represents $\cdot N(R_1) \cdot$, a sulfur atom, an oxygen atom, a selenium atom, or $\cdot (R_2)C=C(R_3) \cdot$; R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a heterocyclic group;

[0014]

Formula (1b)

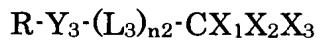


wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a

substituent, provided that at least one of X₁, X₂ and X₃ is a halogen atom; L₂ represents a carbonyl group or a sulfinyl group; Y₂ represents ·N(R₁)·, a sulfur atom, an oxygen atom, a selenium atom, or ·(R₂)C=C(R₃)·; R₁, R₂ and R₃ each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a heterocyclic group; and

[0015]

Formula (1c)



wherein, X₁, X₂ and X₃ each independently represent a hydrogen atom or a substituent, provided that at least one of X₁, X₂ and X₃ is a halogen atom; L₃ represents a sulfonyl group, a carbonyl group or a sulfinyl group; n2 represents 2 or 3; Y₃ represents a single bond, ·N(R₁)·, a sulfur atom, an oxygen atom, a selenium atom, or ·(R₂)C=C(R₃)·; R₁, R₂ and R₃ each independently represent a hydrogen atom or a substituent; and R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group or a heterocyclic group.

[0016]

<2> An image forming method according to <1>, wherein, in Formulae (1a), (1b) and (1c), R is an alkyl group.

<3> An image forming method according to <1> or <2>, wherein, in Formulae (1a), (1b) and (1c), at least one of X₁, X₂ and X₃ is Br.

<4> An image forming method according to any of <1> to <3>, wherein, in Formula (1a), Y₁ is ·N(R₁)·.

<5> An image forming method according to <4>, wherein, in Formula (1a), R₁ is an alkyl group.

[0017]

<6> An image forming method according to any of <1> to <3>, wherein, in Formula (1b), Y₂ is -N(R₁)-.

<7> An image forming method according to <6>, wherein, in Formula (1b), R₁ is a hydrogen atom.

<8> An image forming method according to any of <1> to <3>, wherein, in Formula (1c), Y₃ is a single bond.

<9> An image forming method according to any of <1> to <3>, and <8>, wherein, in Formula (1c), n₂ represents 2.

<10> An image forming method according to any of <1> to <9>, wherein, in Formulae (1a), (1b) and (1c), R and R₁, or R and R₃ form a ring.

<11> An image forming method according to <10>, wherein the ring is an alicyclic group.

[0018]

<12> An image forming method according to any of <1> to <11>, wherein the distance between the scanning line and the insertion part of the thermal developing portion is 45 cm or less.

<13> An image forming method according to any of <1> to <12>, wherein the photothermographic material has a silver coating amount of 1.9 g or less per 1 m² of the photothermographic material.

<14> An image forming method according to any of <1> to <13>, wherein thermal

development is carried out for 6 seconds to 14 seconds.

[0019]

[Embodiments]

The invention will be described in detail below.

The image forming method of the invention is directed to an image forming method for forming an image with an image recording apparatus including laser irradiation means for scan exposing, with a laser beam, a photothermographic material comprising a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder on at least one surface of a support, and means for transporting the photothermographic material in a sub scanning direction and guiding it to a thermal developing portion

[0020]

Preferable components of the photothermographic material of the invention and the image forming method of the invention will be described in detail below.

[0021]

1. Photothermographic material

The photothermographic material of the present invention has an image forming layer comprising at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder on at least one surface of a support, and further comprises a compound represented by formulae

(1a), (1b) or (1c). Further, the image forming layer may have disposed thereon a surface protective layer, or a back layer, a back protective layer and the like may be disposed on an opposite surface of the photothermographic material.

[0022]

1-1. Compound represented by formulae (1a), (1b) or (1c)

The compounds represented by formulae (1a), (1b) or (1c) in the embodiment of the present invention are described below.

[0023]

Formula (1a)

$R \cdot Y_1 \cdot (L_1)_{n1} \cdot CX_1X_2X_3$

wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom. L_1 represents a sulfonyl group. $n1$ represents 0 or 1. Y_1 represents $-N(R_1) \cdot$, a sulfur atom, an oxygen atom, a selenium atom, or $-(R_2)C=C(R_3) \cdot$, and R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent. R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group, or a heterocyclic group.

[0024]

Formula (1b)

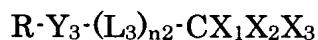
$R \cdot Y_2 \cdot L_2 \cdot CX_1X_2X_3$

wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 is a halogen atom. L_2

represents a carbonyl group or a sulfinyl group. Y_2 represents $-N(R_1)\cdot$, a sulfur atom , an oxygen atom, a selenium atom, or $-(R_2)C=C(R_3)\cdot$, and R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent. R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group, or a heterocyclic group.

[0025]

Formula (1c)



wherein, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 represents a halogen atom. L_3 represents a sulfonyl group, a carbonyl group, or a sulfinyl group. $n2$ represents 2 or 3. Y_3 represents a single bond, $-N(R_1)\cdot$, a sulfur atom , an oxygen atom, a selenium atom, or $-(R_2)C=C(R_3)\cdot$, and R_1 , R_2 and R_3 each independently represent a hydrogen atom or a substituent. R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group, or a heterocyclic group.

[0026]

In formulae (1a) and (1b) described above, X_1 , X_2 and X_3 each independently represent a hydrogen atom or a substituent, provided that at least one of X_1 , X_2 and X_3 represents a halogen atom. The halogen atom is F, Cl, Br or I. In the case of more than two or more are substituted, the halogen atoms may be the same or different, preferably, Cl or Br, and more preferably Br.

[0027]

A substituent other than a halogen atom may be any substituent, but is preferably an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an acyl group, an alkoxycarbonyl group, an aryloxy group, an aryloxycarbonyl group, a carbamoyl group, a sulfamoyl group, an acyloxy group, an acylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonylamino group, an ureido group, a phosphoramido group, a sulfinyl group, a hydroxy group, a heterocyclic group. These groups may be further substituted. Among these, an electron-attracting group is preferable, such as an electron-attracting-group-substituted alkyl group, acyl group, alkoxy group, aryloxycarbonyl group, carbamoyl group, sulfamoyl group and etc., and more preferably an electron-attracting-group-substituted alkyl group.

$CX_1X_2X_3$ group preferably is a trihalomethyl group wherein all of X_1 , X_2 and X_3 are halogen atoms, and more preferably a tribromomethyl group wherein all of the halogen atoms are Br.

[0028]

Y_1 and Y_2 each independently represent $-N(R_1)-$, a sulfur atom, an oxygen atom, a selenium atom, or $-(R_2)C=C(R_3)-$. R_1 , R_2 , and R_3 each independently are a hydrogen atom or a substituent. Y_1 and Y_2 independently preferably are $-N(R_1)-$, an oxygen atom, or a vinyl group, and particularly preferably $-N(R_1)-$. In the case where Y_1 represents $-N(R_1)-$ in formula (1a), R_1 is preferably an alkyl group.

R and R_1 , or R and R_3 may bond together to form a ring. The ring is preferably an alicyclic group. The ring may include a heteroatom.

In the case where Y_2 represents $-N(R_1)-$ in formula (1b), R_1 is preferably a hydrogen atom.

[0029]

R represents a hydrogen atom, a halogen atom, an aliphatic group, an aryl group, or a heterocyclic group.

The aliphatic group is a substituted or an unsubstituted aliphatic group, and may be linear, branched, or cyclic alkyl group, alkenyl group, alkynyl group, aryl group, or heterocyclic group.

The alkyl group preferably is a substituted or an unsubstituted alkyl group having 1 to 30 carbon atoms. Preferred examples include methyl, ethyl, n-propyl, isopropyl, t-butyl, n-octyl, eicosyl, 2-chloroethyl, 2-cyanoethyl, 2-ethylhexyl, cyclohexyl, cyclopentyl, 4-n-dodecylcyclohexyl, bicyclo[1,2,2]heptan-2-yl, bicyclo[2,2,2]octan-3-yl, and the like.

Preferred among the alkenyl group is a substituted or an unsubstituted alkenyl group having 2 to 30 carbon atoms. Examples include vinyl, aryl, prenyl, geranyl, oleyl, 2-cyclopenten-1-yl, 2-cyclohexen-1-yl, bicyclo[2,2,1]hept-2-en-1-yl, bicyclo[2,2,2]oct-2-en-4-yl, and the like.

Preferred among the alkenyl group is a substituted or an unsubstituted alkenyl group having 2 to 30 carbon atoms. Examples include ethynyl, propargyl, a trimethylsilylethyl group and the like.

Preferred among the aryl group represents a substituted or an unsubstituted aryl group having 6 to 30 carbon atoms. Examples can include phenyl, p-tolyl, naphtyl, m-chlorophenyl, o-hexadecanylaminophenyl, and the like.

The heterocyclic group is preferably an aromatic or non-aromatic five or

six-membered heterocyclic group, wherein the heterocyclic group means a univalent heterocyclic group derived from a heterocyclic compound by removal of one hydrogen atom. Examples can include a furyl group, a thienyl group, a pyrimidyl group, a benzothiazolyl group, a pyridyl group, a triazinyl group, a thiazol group, a benzothiazol group, an oxazolyl group, a benzoxazol group, an imidazolyl group, a pyrazolyl group, an indazol group, an indol group, a purine group, a quinoline group, an isoquinoline group, a quinazoline group, a piperidyl group and the like.

[0030]

In the aforementioned formulae (1a) and (1b), R preferably is an aliphatic group, an aryl group, or a heterocyclic group, more preferably an alkyl group or an aryl group, and particularly preferably an alkyl group. In the case that R is an aliphatic group, an aryl group or a heterocyclic group, R may preferably be further substituted with a $-Y_1 \cdot (L_1)_{n1} \cdot CX_1X_2X_3$ group or a $-Y_2 \cdot L_2 \cdot CX_1X_2X_3$ group. In this case, R preferably has additionally from one to three $-Y_1 \cdot (L_1)_{n1} \cdot CX_1X_2X_3$ groups in formula (1a), and R preferably has additionally from one to three $-Y_2 \cdot L_2 \cdot CX_1X_2X_3$ groups in formula (1b), wherein each of Y_1 , L_1 , $n1$, X_1 , X_2 , X_3 , Y_2 and L_2 represent the same as those in formulae (1a) and (1b).

[0031]

L_1 represents a sulfonyl group, and L_2 represents a carbonyl group or a sulfinyl group. $n1$ represents 0 or 1, and preferably 1.

[0032]

The compounds represented by formula (1c) are described below. In formula (1c), X₁, X₂, X₃ and R represent the same as defined in formulae (1a) and (1b), and preferable range of R is also the same as defined therein.

[0033]

In the case that R is an aliphatic group, an aryl group, or a heterocyclic group, R preferably has several (preferably 2 or 4) –Y₃·(L₃)_{n2}·CX₁X₂X₃, wherein, each of Y₃, n2, X₁, X₂, X₃ and L₃ are the same as those in formula (1c).

[0034]

Y₃ in formula (1c) represents a single bond, –N(R₁)·, a sulfur atom, an oxygen atom, a selenium atom, or –(R₂)C=C(R₃)·. R₁, R₂ and R₃ each independently represent a hydrogen atom, or a substituent. Y₃ represents preferably a single bond, –N(R₁)·, an oxygen atom, or a vinyl group, and more preferably a single bond or –N(R₁)·. In the case that Y₃ is –N(R₁)·, R₁ preferably represents an alkyl group or a hydrogen atom.

R and R₁ or R and R₃ may bond together to form a ring, and preferably an alicyclic group. The ring may include a heteroatom. L₃ represents a sulfonyl group, a carbonyl group, or a sulfinyl group, and more preferably a sulfonyl group. n₂ represents 2 or 3, and preferably 2.

[0035]

In the present invention, more preferable compound among the compounds represented by formulae (1a) to (1c) is a compound represented by formulae (1a) or (1b), and particularly preferable is a compound described

represented by formula (1b).

[0036]

Halogeno compounds represented by formulae (1a) to (1c) may comprise a ballasted group, wherein the ballasted group means a substituent having 8 or more carbon atoms in total, preferably 8 to 100 carbon atoms, more preferably 8 to 60 carbon atoms, and further more preferably 10 to 40 carbon atoms. Preferable ballasted group include an aliphatic hydrocarbon group (for example, an alkyl group, an alkenyl group, an alkynyl group and etc), an aryl group, a heterocyclic group, or combination of these groups with an ether group, a thioether group, a carbonyl group, an amino group, a sulfonyl group, and a phosphonyl group. The ballasted group may represent a polymer. Practical examples of ballasted group are described, for example, in Research Disclosure, 1995/2, 37938, pages 82 to 89, JP-A Nos. 1-280747, and 1-283548.

The ballasted group may be added as a substituent represented by the aforementioned R_1 , R_2 and R_3 , or as an aliphatic group represented by R , or as a substituent represented by X_1 , X_2 , and X_3 .

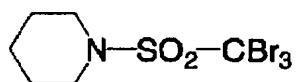
[0037]

Specific examples of the compound represented by formulae (1a) to (1c) are described below. However, the present invention is not limited thereto.

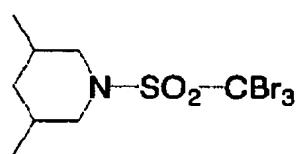
[0038]

[Formula 1]

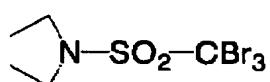
1a-1



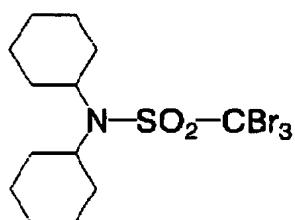
1a-2



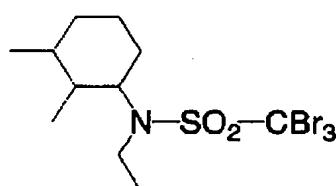
1a-3



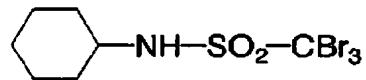
1a-4



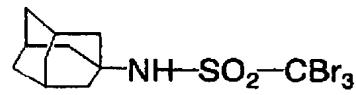
1a-5



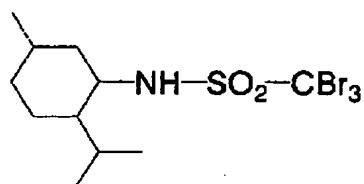
1a-6



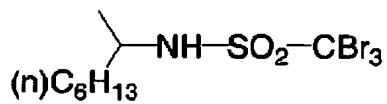
1a-7



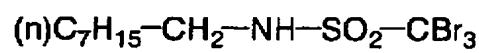
1a-8



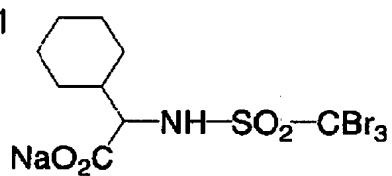
1a-9



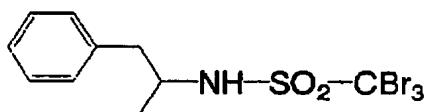
1a-10



1a-11



1a-12



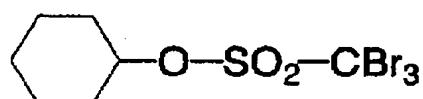
[0039]

[Formula 2]

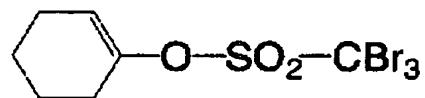
1a-13



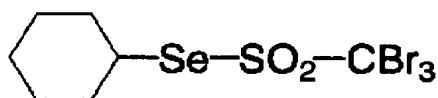
1a-14



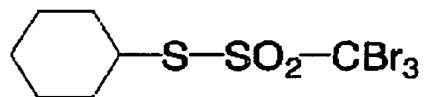
1a-15



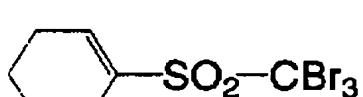
1a-16



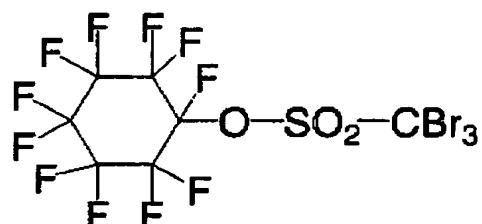
1a-17



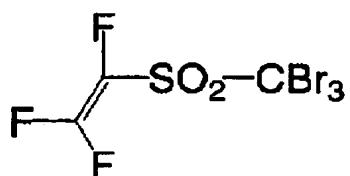
1a-18



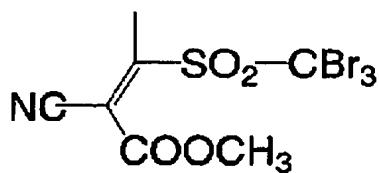
1a-19



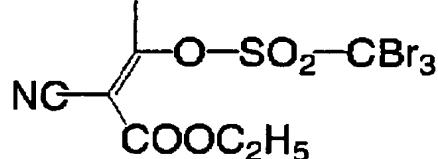
1a-20



1a-21



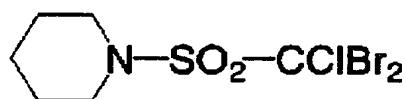
1a-22



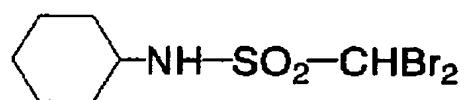
[0040]

[Formula 3]

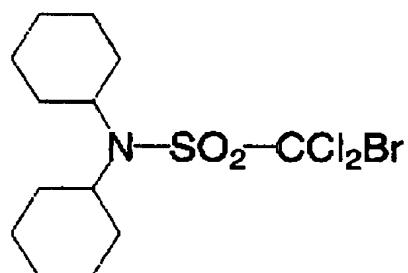
1a-23



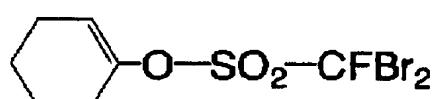
1a-24



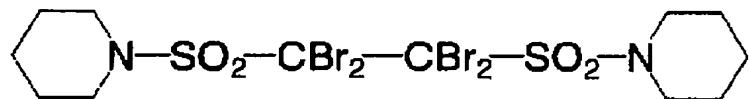
1a-25



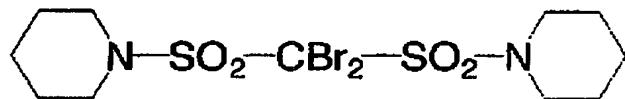
1a-26



1a-27



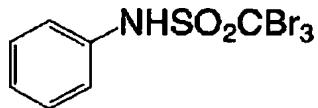
1a-28



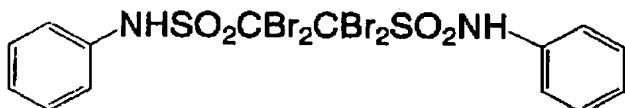
[0041]

[Formula 4]

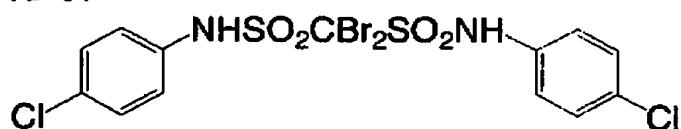
1a-29



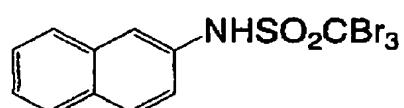
1a-30



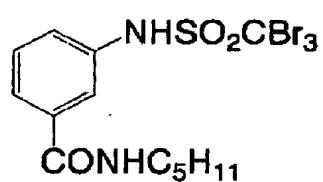
1a-31



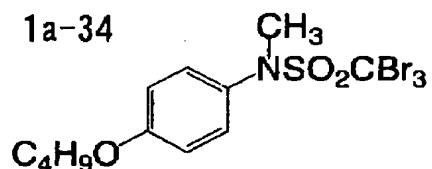
1a-32



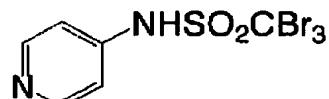
1a-33



1a-34



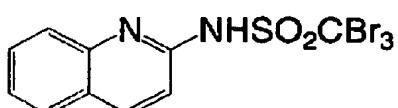
1a-35



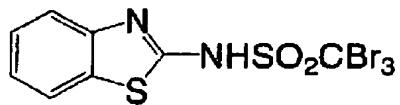
1a-36



1a-37

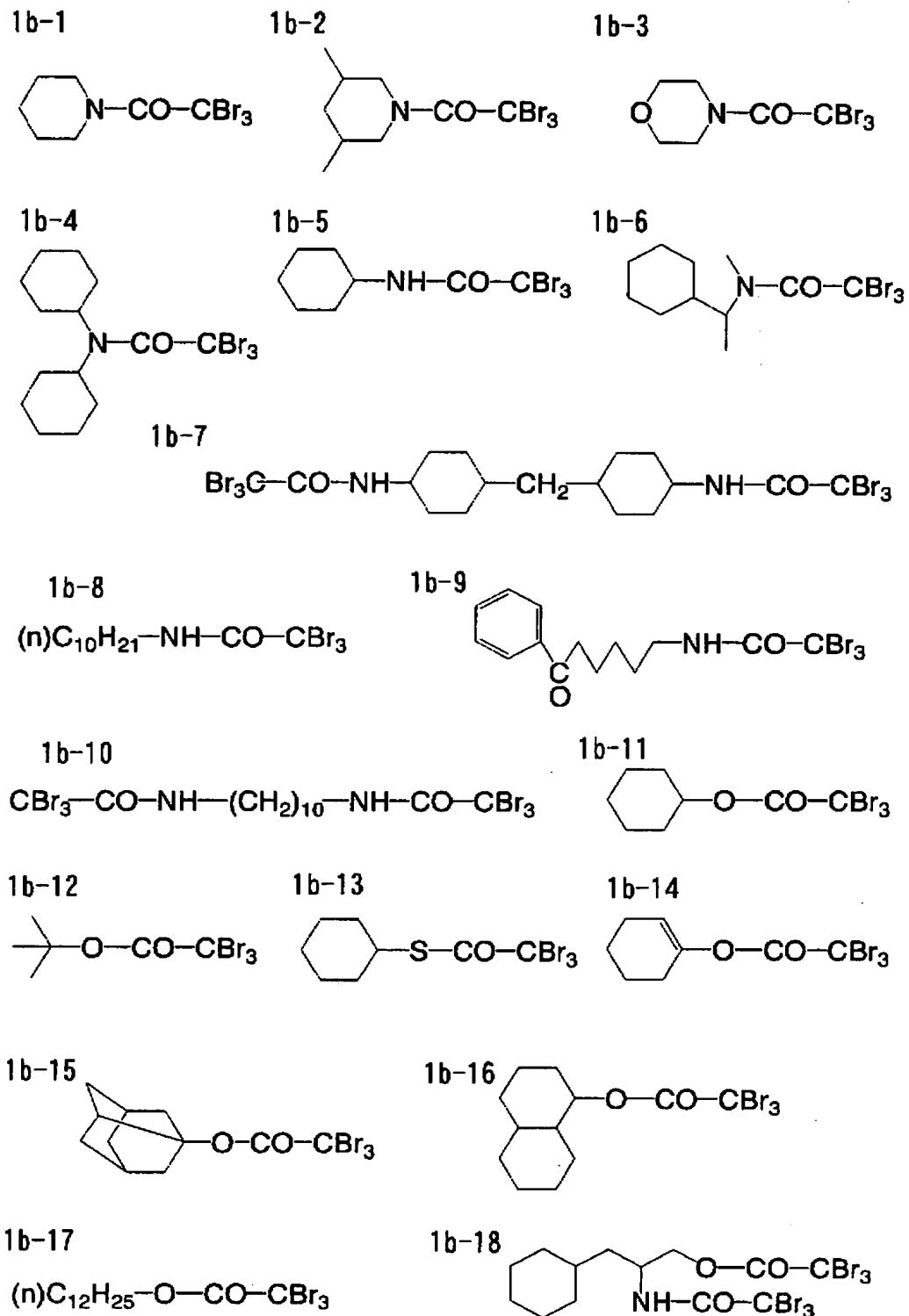


1a-38



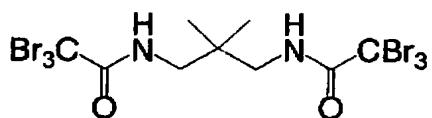
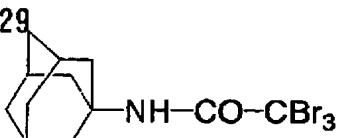
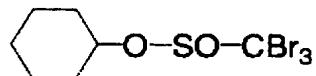
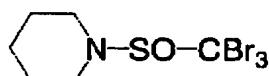
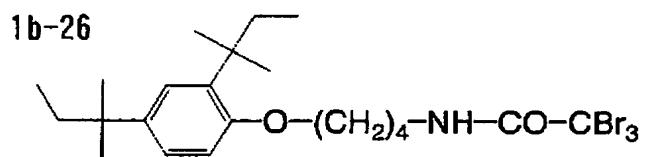
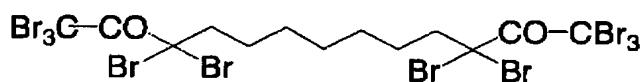
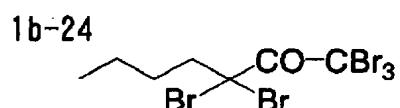
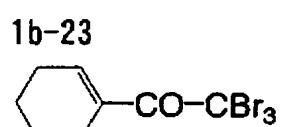
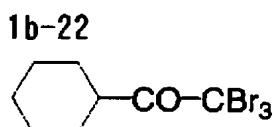
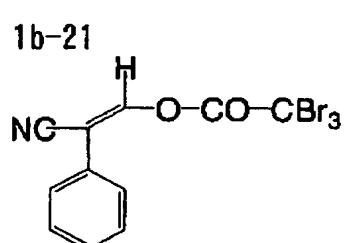
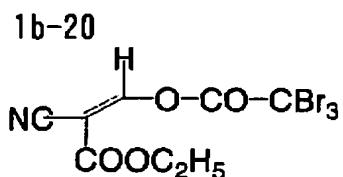
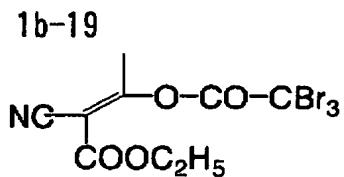
[0042]

[Formula 5]



[0043]

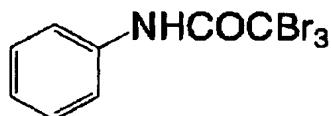
[Formula 6]



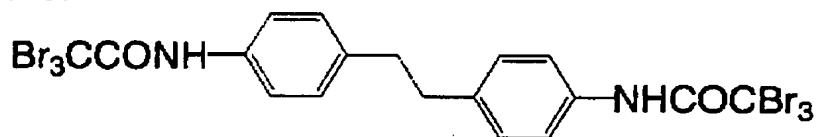
[0044]

[Formula 7]

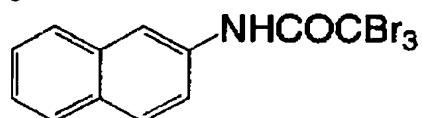
1b-31



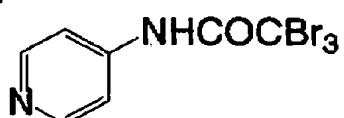
1b-32



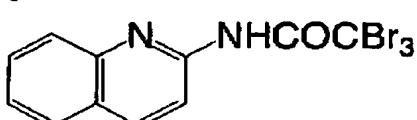
1b-33



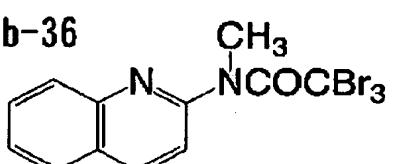
1b-34



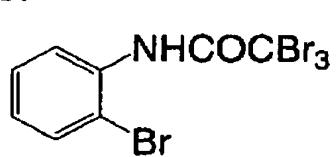
1b-35



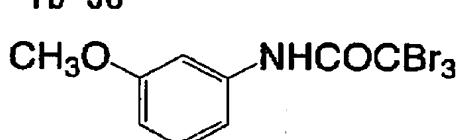
1b-36



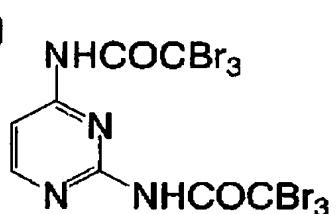
1b-37



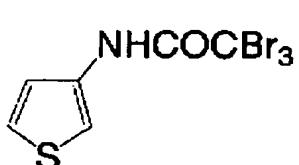
1b-38



1b-39



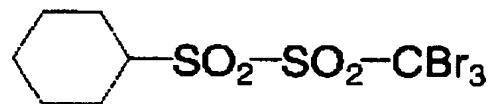
1b-40



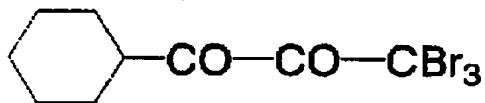
[0045]

[Formula 8]

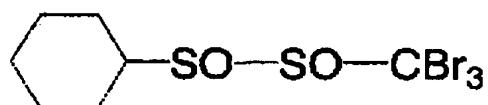
1c-1



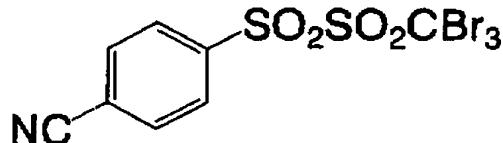
1c-2



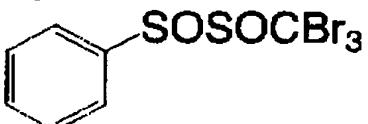
1c-3



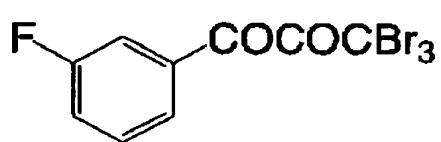
1c-4



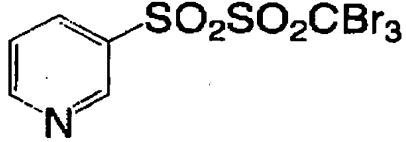
1c-5



1c-6



1c-7



[0046]

The compound represented by formulae (1a), (1b) or (1c) is preferably added in an image forming layer, and more preferably is added during the preparation of a coating solution for image forming layer. In the case the compound is added at the preparation of a coating solution for image forming layer, the compound may be added during any step of the process, for example, at

a silver halide grain formation step, before initiating a desalting step, during a desalting step, before a chemical ripening step, during a chemical ripening step, and before preparation of a final emulsion step. Addition may be conducted in several times during these steps. The compound is preferably added to the image forming layer. The compound may be added to a surface protective layer or an intermediate layer which are adjacent to the image forming layer, as well as the image forming layer, to be diffused to the image forming layer in the coating step.

Preferable addition amount is fairly dependent on the aforementioned addition method or addition compounds, and is generally 1×10^{-4} mol to 0.8 mol, preferably 1×10^{-3} mol to 0.1 mol, and still more preferably 5×10^{-3} mol to 0.05 mol per one mol of a non-photosensitive organic silver salt.

[0047]

The compound of the invention may be added as a solution in a water-soluble solvent, such as, water, methanol, ethanol or mixtures thereof. In this case, pH may be controlled with acid or base, or a surfactant may be also used. The compounds may be dissolved in a high boiling organic solvent as an emulsified dispersion. Further the compound can be added as a solid dispersion.

[0048]

1-2. Non-photosensitive organic silver salt

1) Composition

The organic silver salt particle according to the invention is relatively stable to light but serves as to supply silver ions and forms silver images when

heated to 80°C or higher under the presence of an exposed photosensitive silver halide and a reducing agent. The organic silver salt may be any organic material containing a source capable of reducing silver ions. Such non-photosensitive organic silver salt is disclosed, for example, in JP-A No. 10-62899 (paragraph Nos. 0048 to 0049), EP-A No. 0803764A1 (page 18, line 24 to page 19, line 37), EP-A No. 962812A1, JP-A Nos. 11-349591, 2000-7683, and 2000-72711, and the like. A silver salt of organic acid, particularly, a silver salt of long chained fatty acid carboxylic acid (having 10 to 30 carbon atoms, preferably, 15 to 28 carbon atoms) is preferable. Preferred examples of the silver salt of the organic acid can include, for example, silver lignocerate, silver behenate, silver arachidinate, silver stearate, silver oleate, silver laurate, silver capronate, silver myristate, silver palmitate, silver erucate and mixtures thereof.

[0049]

Among the organic silver salts, it is preferred to use an organic silver salt with the silver behenate content of 50 mol% or more, more preferably, 85 mol% or more, further preferably, 95 mol% or more. And, it is preferred to use an organic silver salt with the silver erucate content of 2 mol% or less, more preferably, 1 mol% or less, further preferably, 0.1 mol% or less. It is preferred that the content of the silver stearate is 1 mol% or less. When the content of the silver stearate is 1 mol% or less, a silver salt of organic acid having low Dmin, high sensitivity and excellent image stability can be obtained. The content of the silver stearate above-mentioned, is preferably 0.5 mol% or less, more preferably, the silver stearate is not substantially contained.

[0050]

Further, in the case the silver salt of organic acid includes silver arachidinic acid, it is preferred that the content of the silver arachidinic acid is 6 mol% or less in order to obtain a silver salt of organic acid having low Dmin and excellent image stability. The content of the silver arachidinate is more preferably 3 mol% or less.

[0051]

2) Shape

There is no particular restriction on the shape of the organic silver salt usable in the invention and it may needle-like, bar-like, plate-like or flaky shape.

In the invention, a flaky shaped organic silver salt is preferred. Short needle-like, rectangular, cuboidal or potato-like indefinite shaped particle with the major axis to minor axis ratio being 5 or less is also used preferably. Such organic silver particle has a feature less suffering from fogging during thermal development compared with long needle-like particles with the major axis to minor axis length ratio of 5 or more. Particularly, a particle with the major axis to minor axis ratio of 3 or less is preferred since it can improve the mechanical stability of the coating film. In the present specification, the flaky shaped organic silver salt is defined as described below. When an organic acid silver salt is observed under an electron microscope, calculation is made while approximating the shape of an organic acid silver salt particle to a rectangular body and assuming each side of the rectangular body as a, b, c from the shorter side (c may be identical with b) and determining x based on numerical values a, b for the shorter side as below.

$$x = b/a$$

[0052]

As described above, x is determined for the particles by the number of about 200 and those capable of satisfying the relation: x (average) ≥ 1.5 as an average value x is defined as a flaky shape. The relation is preferably: $30 \geq x$ (average) ≥ 1.5 and, more preferably, $15 \geq x$ (average) ≥ 1.5 . By the way, needle-like is expressed as $1 \leq x$ (average) < 1.5 .

[0053]

In the flaky shaped particle, a can be regarded as a thickness of a plate particle having a main plate with b and c being as the sides. a in average is preferably $0.01 \mu\text{m}$ to $0.3 \mu\text{m}$ and, more preferably, $0.1 \mu\text{m}$ to $0.23 \mu\text{m}$. c/b in average preferably 1 to 9, more preferably, 1 to 6 and, further preferably, 1 to 4 and, most preferably, 1 to 3.

[0054]

By controlling the sphere equivalent diameter to $0.05 \mu\text{m}$ to $1 \mu\text{m}$, it causes less agglomeration in the photosensitive material and image stability is improved. The spherical equivalent diameter is preferably $0.1 \mu\text{m}$ to $1 \mu\text{m}$. In the invention, the sphere equivalent diameter can be measured by a method of photographing a sample directly by using an electron microscope and then image-processing negative images.

[0055]

In the flaky shaped particle, the sphere equivalent diameter of the particle/a is defined as an aspect ratio. The aspect ratio of the flaky particle is, preferably, 1.1 to 30 and, more preferably, 1.1 to 15 with a viewpoint of causing less agglomeration in the photosensitive material and improving the image stability.

[0056]

As the particle size distribution of the organic silver salt, mono-dispersion is preferred. In the mono-dispersion, the percentage for the value obtained by dividing the standard deviation for the length of minor axis and major axis by the minor axis and the major axis respectively is, preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. The shape of the organic silver salt can be measured by determining dispersion of an organic silver salt as transmission type electron microscopic images. Another method of measuring the mono-dispersion is a method of determining of the standard deviation of the volume weighted mean diameter of the organic silver salt in which the percentage for the value defined by the volume weight mean diameter (variation coefficient), is preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. The mono-dispersion can be determined from particle size (volume weighted mean diameter) obtained, for example, by a measuring method of irradiating a laser beam to an organic silver salt dispersed in a liquid, and determining a self correlation function of the fluctuation of scattered light to the change of time.

[0057]

3) Preparing method

Methods known in the art may be applied to the method for producing the organic silver salt used in the invention, and to the dispersion method thereof. For example, reference can be made to JP-A No. 10-62899, EP-A Nos. 0803763A1 and 0962812A1, JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2001-163889, 2001-163890, 2001-163827, 2001-33907, 2001-188313, 2001-83652, 2002-6442, 2002-49117, 2002-31870 and 2002-107868.

[0058]

When a photosensitive silver salt is present together during dispersion of the organic silver salt, fog increases and the sensitivity becomes remarkably lower, so that it is more preferred that the photosensitive silver salt is not substantially contained during dispersion. In the invention, the amount of the photosensitive silver salt to be disposed in the aqueous dispersion, is preferably, 1 mol% or less, more preferably, 0.1 mol% or less per one mol of the organic acid silver salt in the solution and, further preferably, positive addition of the photosensitive silver salt is not conducted.

[0059]

In the invention, the photosensitive material can be prepared by mixing an aqueous dispersion of an organic silver salt and an aqueous dispersion of a photosensitive silver salt and the mixing ratio between the organic silver salt and the photosensitive silver salt can be selected depending on the purpose. The ratio of the photosensitive silver salt to the organic silver salt is, preferably, in the range from 1 mol% to 30 mol%, more preferably, in the range from 2 mol% to

20 mol% and, particularly preferably, 3 mol% to 15 mol%. A method of mixing two or more kinds of aqueous dispersions of organic silver salts and two or more kinds of aqueous dispersions of photosensitive silver salts upon mixing are used preferably for controlling the photographic properties.

[0060]

4) Addition amount

While an organic silver salt in the invention can be used in a desired amount, an amount of an organic silver salt is preferably in the range from 0.6 g/m² to 1.9 g/m², and to improve the image stability, more preferably from 0.8 g/m² to 1.5 g/m² and further preferably from 1.0 g/m² to 1.5 g/m² with respect to a total coating amount of silver including silver halide.

[0061]

1-3. Reducing agent

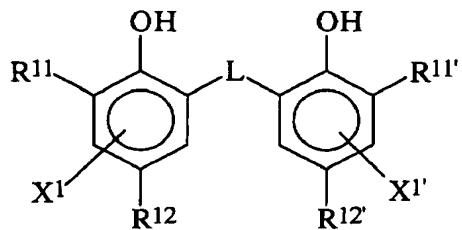
The photothermographic material of the invention contains a reducing agent for the organic silver salt. The reducing agent may be any substance (preferably, organic substance) capable of reducing silver ions into metallic silver. Examples of the reducing agent are described in JP-A No. 11-65021 (column Nos. 0043 to 0045) and EP-A 0803764 A1 (p. 7, line 34 to p. 18, line 12).

In the invention, a so-called hindered phenolic reducing agent or a bisphenol agent having a substituent at the ortho-position to the phenolic hydroxyl group is preferred and the compound represented by the following formula (R) is more preferred.

[0062]

Formula (R)

[Formula 9]



[0063]

In formula (R), R^{11} and $R^{11'}$ each independently represent an alkyl group having 1 to 20 carbon atoms. R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. L represents a $-S-$ group or a $-CHR^{13}-$ group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms. X^1 and $X^{1'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

[0064]

Each of the substituents is to be described specifically.

1) R^{11} and $R^{11'}$

R^{11} and $R^{11'}$ each independently represent a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms. The substituent for the alkyl group has no particular restriction and can include, preferably, aryl group, hydroxy group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, acyl group,

carbamoyl group, ester group, and halogen atom.

[0065]

2) R^{12} and $R^{12'}$, X^1 and $X^{1'}$

R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. X^1 and $X^{1'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. Each of the groups capable of substituting for a hydrogen atom on the benzene ring can include, preferably, alkyl group, aryl group, halogen atom, alkoxy group, and acylamino group.

[0066]

3) L

L represents a $-S-$ group or a $-CHR^{13}-$ group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms in which the alkyl group may have a substituent. Specific examples of the non-substituted alkyl group for R^{13} can include, for example, methyl group, ethyl group, propyl group, butyl group, heptyl group, undecyl group, isopropyl group, 1-ethylpentyl group, and 2,4,4-trimethylpentyl group. Examples of the substituent for the alkyl group can include, like substituent R^{11} , a halogen atom, an alkoxy group, alkylthio group, aryloxy group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, oxycarbonyl group, carbamoyl group, and sulfamoyl group.

[0067]

4) Preferred substituents

R^{11} and $R^{11'}$ are, preferably, a secondary or tertiary alkyl group having 3 to 15 carbon atoms and can include, specifically, isopropyl group, isobutyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, cyclopentyl group, 1-methylcyclohexyl group, and 1-methylcyclopropyl group. R^{11} and $R^{11'}$ each represents, more preferably, tertiary alkyl group having 4 to 12 carbon atoms and, among them, t-butyl group, t-amyl group, 1-methylcyclohexyl group are further preferred, t-butyl group being most preferred.

[0068]

R^{12} and $R^{12'}$ are, preferably, alkyl groups having 1 to 20 carbon atoms and can include, specifically, methyl group, ethyl group, propyl group, butyl group, isopropyl group, t-butyl group, t-amyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, methoxymethyl group and methoxyethyl group. More preferred are methyl group, ethyl group, propyl group, isopropyl group, and t-butyl group.

X^1 and $X^{1'}$ are, preferably, a hydrogen atom, halogen atom, or alkyl group, and more preferably, hydrogen atom.

[0069]

L is preferably a group $\cdot\text{CHR}^{13}\cdot$.

R^{13} is, preferably, a hydrogen atom or an alkyl group having 1 to 15 carbon atoms. The alkyl group is preferably methyl group, ethyl group, propyl group, isopropyl group and 2,4,4-trimethylpentyl group. Particularly preferred R^{13} is a hydrogen atom, methyl group, propyl group or isopropyl group.

[0070]

In a case where R^{13} is a hydrogen atom, R^{12} and $R^{12'}$ each represent, preferably, an alkyl group having 2 to 5 carbon atoms, ethyl group and propyl group being more preferred and ethyl group being most preferred.

In a case where R^{13} is a primary or secondary alkyl group having 1 to 8 carbon atom, R^{12} and $R^{12'}$ each represent preferably methyl group. As the primary or secondary alkyl group of 1 to 8 carbon atoms for R^{13} , methyl group, ethyl group, propyl group and isopropyl group are more preferred, and methyl group, ethyl group, and propyl group are further preferred.

In a case where each of R^{11} , $R^{11'}$ and R^{12} , $R^{12'}$ is methyl group, R^{13} is preferably a secondary alkyl group. In this case, the secondary alkyl group for R^{13} is preferably isopropyl group, isobutyl group and 1-ethylpentyl group, with isopropyl group being more preferred.

The reducing agent described above shows different thermal developing performances or developed-silver tones or the like depending on the combination of R^{11} , $R^{11'}$ and R^{12} , $R^{12'}$, as well as R^{13} . Since these performances can be controlled by using two or more kinds of reducing agents at various mixing ratios, it is preferred to use two or more kinds of reducing agents in combination depending on the purpose.

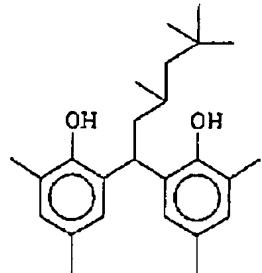
[0071]

Specific examples of the reducing agents of the invention including the compounds represented by formula (R) according to the invention are shown below, but the invention is not restricted to them.

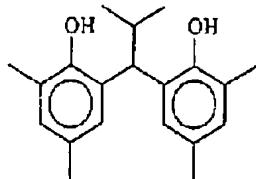
[0072]

[Formula 10]

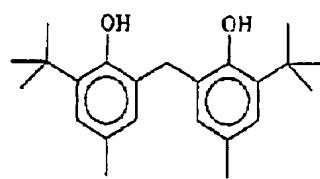
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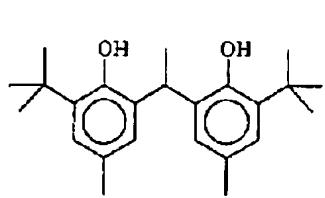
(R - 2)



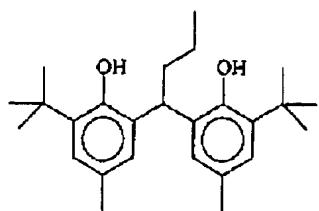
(R - 3)



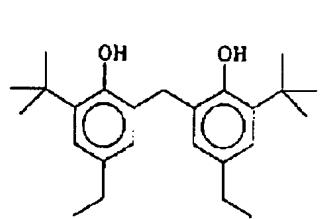
(R - 4)



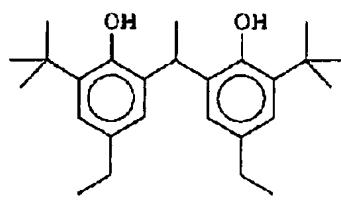
(R - 5)



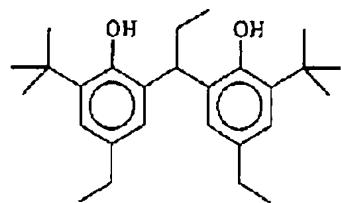
(R - 6)



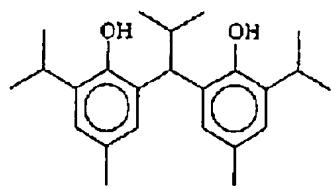
(R - 7)



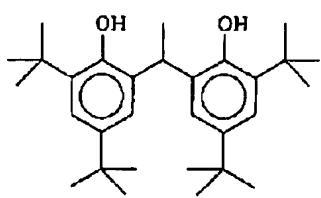
(R - 8)



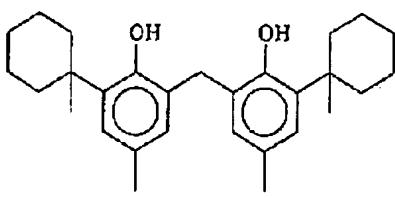
(R - 9)



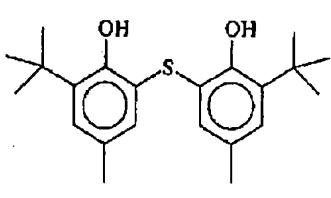
(R - 10)



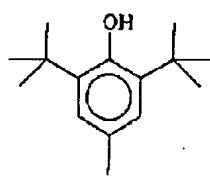
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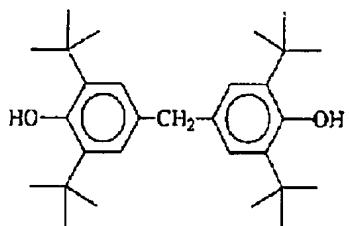
(R - 12)



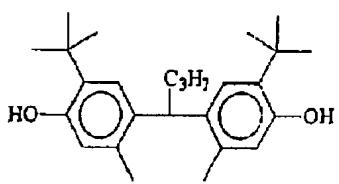
(R - 13)



(R - 14)



(R - 15)



[0073]

As preferred reducing agents of the invention other than those above, there can be mentioned compounds disclosed in JP-A Nos. 2001-188314, 2001-209145, 2001-350235, and 2002-156727.

In the invention, the addition amount of the reducing agent is, preferably, from 0.1 g/m² to 3.0 g/m², more preferably, 0.2 g/m² to 1.5 g/m² and, further preferably 0.3 g/m² to 1.0 g/m². It is, preferably, contained by 5 mol% to 50 mol%, more preferably, 8 mol% to 30 mol% and, further preferably, 10 mol% to 20 mol% per one mole of silver in the image forming layer. The reducing agent of the invention is preferably contained in the image forming layer.

[0074]

In the invention, the reducing agent may be incorporated into photosensitive material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid particle dispersion, and the like.

As a well known emulsion dispersion method, there can be mentioned a method comprising dissolving the reducing agent in an auxiliary solvent such as oil, for instance, dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, diethyl phthalate, and the like, as well as ethyl acetate, cyclohexanone, and the like; from which an emulsion dispersion is mechanically produced.

[0075]

As solid particle dispersion method, there can be mentioned a method comprising dispersing the powder of the reducing agent in a proper medium such

as water, by means of ball mill, colloid mill, vibrating ball mill, sand mill, jet mill, roller mill, or ultrasonics, thereby obtaining solid dispersion. In this case, there can also be used a protective colloid (such as polyvinyl alcohol), or a surfactant (for instance, an anionic surfactant such as sodium triisopropylnaphthalenesulfonate (a mixture of compounds having the isopropyl groups in different substitution sites)). In the mills enumerated above, generally used as the dispersion media are beads made of zirconia and the like, and Zr and the like eluting from the beads may be incorporated in the dispersion. Although depending on the dispersing conditions, the amount of Zr and the like generally incorporated in the dispersion is in the range of from 1 ppm to 1000 ppm. It is practically acceptable so long as Zr is incorporated in an amount of 0.5 mg or less per 1 g of silver. Preferably, a preservative (for instance, sodium benzoisothiazolinone salt) is added in the water dispersion.

In the invention, furthermore, the reducing agent is preferably used as solid dispersion, and is added in the form of fine particles having average particle size from 0.01 μm to 10 μm , and more preferably, from 0.05 μm to 5 μm and, further preferably, from 0.1 μm to 2 μm . In the invention, other solid dispersions are preferably used with this particle size range.

[0076]

1·4. Development accelerator

In the photothermographic material of the invention, sulfoneamide phenolic compounds described in the specification of JP·A No. 2000·267222, and represented by formula (A) described in the specification of JP·A No. 2000·330234; hindered phenolic compounds represented by formula (II) described in

JP-A No. 2001-92075; hydrazine compounds described in the specification of JP-A No. 10-62895, represented by formula (I) described in the specification of JP-A No. 11-15116, represented by formula (D) described in the specification of JP-A No. 2002-156727, and represented by formula (1) described in the specification of Japanese Patent Application No. 2001-074278; and phenolic or naphthalic compounds represented by formula (2) described in the specification of JP-A No. 2001-264929 are used preferably as a development accelerator. The development accelerator described above is used in the range from 0.1 mol% to 20 mol%, preferably, in the range from 0.5 mol% to 10 mol% and, more preferably, in the range from 1 mol% to 5 mol% with respect to the reducing agent. The introduction methods to the photothermographic material can include, the same methods as those for the reducing agent and, it is particularly preferred to add as a solid dispersion or an emulsion dispersion. In a case of adding as an emulsion dispersion, it is preferred to add as an emulsion dispersion dispersed by using a high boiling solvent which is solid at a normal temperature and an auxiliary solvent at a low boiling point, or to add as a so-called oilless emulsion dispersion not using the high boiling solvent.

[0077]

In the present invention, it is more preferred to use as a development accelerator, hydrazine compounds represented by formula (D) described in the specification of JP-A No. 2002-156727, and phenolic or naphthalic compounds represented by formula (2) described in the specification of JP-A No. 2001-264929.

[0078]

Particularly preferred development accelerators of the invention are compounds represented by the following formulae (A-1) and (A-2).

[0079]

Formula (A-1)

$Q_1\text{-NHNH-}Q_2$

(wherein, Q_1 represents an aromatic group or a heterocyclic group coupling at a carbon atom to $\text{-NHNH-}Q_2$ and Q_2 represents a carbamoyl group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a sulfonyl group or a sulfamoyl group).

[0080]

In formula (A-1), the aromatic group or the heterocyclic group represented by Q_1 is, preferably, 5 to 7 membered unsaturated ring. Preferred examples are benzene ring, pyridine ring, pyrazine ring, pyrimidine ring, pyridazine ring, 1,2,4-triazine ring, 1,3,5-triazine ring, pyrrole ring, imidazole ring, pyrazole ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, 1,2,5-oxadiazole ring, thiazole ring, oxazole ring, isothiazole ring, isooxazole ring, and thiophene ring. Condensed rings in which the rings described above are condensed to each other are also preferred.

[0081]

The rings described above may have substituents and in a case where they have two or more substituents, the substituents may be identical or

different with each other. Examples of the substituents can include halogen atom, alkyl group, aryl group, carboamide group, alkylsulfoneamide group, arylsulfonamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, carbamoyl group, sulfamoyl group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, aryloxycarbonyl group and acyl group.

In a case where the substituents are groups capable of substitution, they may have further substituents and examples of preferred substituents can include halogen atom, alkyl group, aryl group, carbonamide group, alkylsulfoneamide group, arylsulfoneamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, cyano group, sulfamoyl group, alkylsulfonyl group, arylsulfonyl group and acyloxy group.

[0082]

The carbamoyl group represented by Q_2 is a carbamoyl group preferably having 1 to 50 carbon atoms and, more preferably, having 6 to 40 carbon atoms, and examples can include not-substituted carbamoyl, methyl carbamoyl, N-ethylcarbamoyl, N-propylcarbamoyl, N-sec-butylcarbamoyl, N-octylcarbamoyl, N-cyclohexylcarbamoyl, N-tert-butylcarbamoyl, N-dodecylcarbamoyl, N-(3-dodecyloxypropyl)carbamoyl, N-octadecylcarbamoyl, N-{3-(2,4-tert-pentylphenoxy)propyl} carbamoyl, N-(2-hexyldecyl)carbamoyl, N-phenylcarbamoyl, N-(4-dodecyloxyphenyl)carbamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)carbamoyl, N-naphthylcarbamoyl, N-3-pyridylcarbamoyl and N-benzylcarbamoyl.

[0083]

The acyl group represented by Q_2 is an acyl group, preferably, having 1 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms and can include, for example, formyl, acetyl, 2-methylpropanoyl, cyclohexylcarbonyl, octanoyl, 2-hexyldecanoyl, dodecanoyl, chloroacetyl, trifluoroacetyl, benzoyl, 4-dodecyloxybenzoyl, and 2-hydroxymethylbenzoyl. Alkoxycarbonyl group represented by Q_2 is an alkoxycarbonyl group, preferably, of 2 to 50 carbon atom and, more preferably, of 6 to 40 carbon atoms and can include, for example, methoxycarbonyl, ethoxycarbonyl, isobutyloxycarbonyl, cyclohexyloxycarbonyl, dodecyloxycarbonyl and benzyloxycarbonyl.

[0084]

The aryloxy carbonyl group represented by Q_2 is an aryloxycarbonyl group, preferably, having 7 to 50 carbon atoms and, more preferably, having 7 to 40 carbon atoms and can include, for example, phenoxy carbonyl, 4-octyloxyphenoxy carbonyl, 2-hydroxymethylphenoxy carbonyl, and 4-dodecyloxyphenoxy carbonyl. The sulfonyl group represented by Q_2 is a sulfonyl group, preferably having 1 to 50 carbon atoms and, more preferably, having 6 to 40 carbon atoms and can include, for example, methylsulfonyl, butylsulfonyl, octylsulfonyl, 2-hexadecylsulfonyl, 3-dodecyloxypropylsulfonyl, 2-octyloxy-5-tert-octylphenyl sulfonyl, and 4-dodecyloxyphenyl sulfonyl.

[0085]

The sulfamoyl group represented by Q_2 is sulfamoyl group, preferably having 0 to 50 carbon atoms, more preferably, 6 to 40 carbon atoms and can

include, for example, not-substituted sulfamoyl, N-ethylsulfamoyl group, N-(2-ethylhexyl)sulfamoyl, N-decylsulfamoyl, N-hexadecylsulfamoyl, N-{3-(2-ethylhexyloxy)propyl}sulfamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)sulfamoyl, and N-(2-tetradecyloxyphenyl)sulfamoyl.

The group represented by Q_2 may further have a group mentioned as the example of the substituent of 5 to 7-membered unsaturated ring represented by Q_1 at the position capable of substitution. In a case where the group has two or more substituents, such substituents may be identical or different with each other.

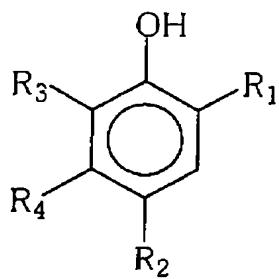
[0086]

Then, preferred range for the compounds represented by formula (A-1) is to be described. 5 to 6 membered unsaturated ring is preferred for Q_1 , and benzene ring, pyrimidine ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, thioazole ring, oxazole ring, isothiazole ring, isooxazole ring and a ring in which the ring described above is condensed with a benzene ring or unsaturated hetero ring are further preferred. Further, Q_2 is preferably a carbamoyl group and, particularly, a carbamoyl group having hydrogen atom on the nitrogen atom is particularly preferred.

[0087]

Formula (A-2)

[Formula 11]



[0088]

In formula (A-2), R₁ represents an alkyl group, an acyl group, an acylamino group, a sulfoneamide group, an alkoxy carbonyl group, or a carbamoyl group. R₂ represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acyloxy group or a carbonate ester group. R₃, R₄ each represents a group capable of substituting for a hydrogen atom on a benzene ring which is mentioned as the example of the substituent for formula (A-1). R₃ and R₄ may bond together to form a condensed ring.

[0089]

R₁ is, preferably, an alkyl group having 1 to 20 carbon atoms (for example, methyl group, ethyl group, isopropyl group, butyl group, tert-octyl group, or cyclohexyl group), an acylamino group (for example, acetylamino group, benzoylamino group, methylureido group, or 4-cyanophenylureido group), a carbamoyl group (for example, n-butylcarbamoyl group, N,N-diethylcarbamoyl group, phenylcarbamoyl group, 2-chlorophenylcarbamoyl group, or 2,4-dichlorophenylcarbamoyl group), an acylamino group (including ureido group or urethane group) being more preferred. R₂ is, preferably, a halogen atom (more

preferably, chlorine atom, bromine atom), an alkoxy group (for example, methoxy group, butoxy group, n-hexyloxy group, n-decyloxy group, cyclohexyloxy group or benzyloxy group), or an aryloxy group (phenoxy group or naphthoxy group).

[0090]

R_3 preferably is a hydrogen atom, a halogen atom or an alkyl group having 1 to 20 carbon atoms, and most preferably a halogen atom. R_4 is preferably a hydrogen atom, alkyl group or an acylamino group, and more preferably an alkyl group or an acylamino group. Examples of the preferred substituent thereof are identical with those for R_1 . In a case where R_4 is an acylamino group, R_4 may preferably bond with R_3 to form a carbostyryl ring.

[0091]

In a case where R_3 and R_4 in formula (A-2) bond together to form a condensed ring, a naphthalene ring is particularly preferred as the condensed ring. The same substituent as the example of the substituent referred to for formula (A-1) may bond to the naphthalene ring. In a case where formula (A-2) is a naphtholic compound, R_1 , is, preferably, a carbamoyl group. Among them, benzoyl group is particularly preferred. R_2 is, preferably, an alkoxy group or an aryloxy group and, particularly, preferably an alkoxy group.

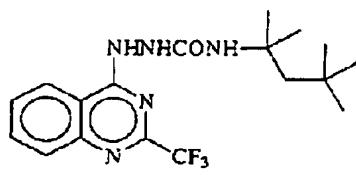
[0092]

Preferred specific examples for the development accelerator of the invention are to be described below. The invention is not restricted to them.

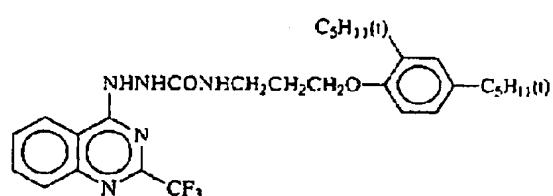
[0093]

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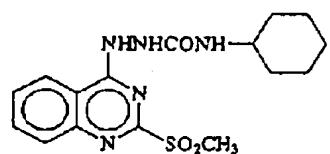
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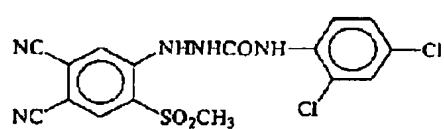
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(A - 3)



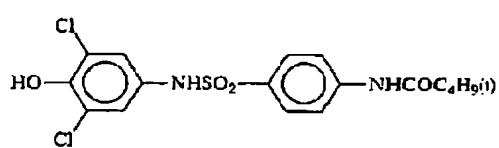
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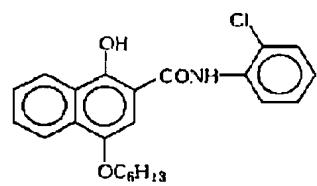
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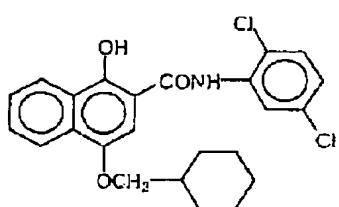
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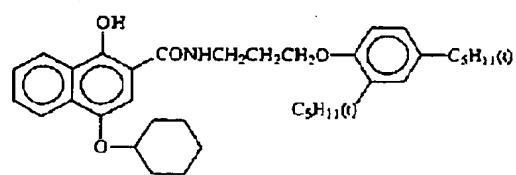
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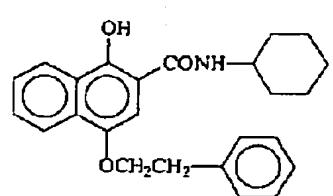
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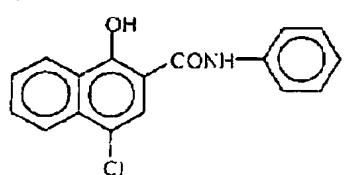
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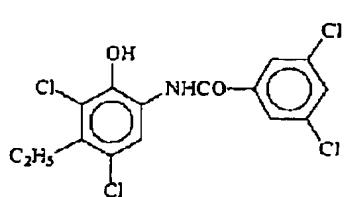
(A - 10)



(A - 11)



(A - 12)



[0094]

1-5. Hydrogen bonding compound

In the invention, in the case that the reducing agent has an aromatic hydroxyl group (-OH) or an amino group (-NHR, R represents each one of hydrogen atom and alkyl group), particularly in the case that the reducing agent is a bisphenol described above, it is preferred to use in combination, a non-reducing compound having a group capable of reacting with these groups of the reducing agent, and that is also capable of forming a hydrogen bond therewith.

[0095]

As a group forming a hydrogen bond with a hydroxyl group or an amino group, there can be mentioned a phosphoryl group, a sulfoxido group, a sulfonyl group, a carbonyl group, an amido group, an ester group, an urethane group, an ureido group, a tertiary amino group, a nitrogen-containing aromatic group, and the like. Particularly preferred among them is phosphoryl group, sulfoxido group, amido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), urethane group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), and ureido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)).

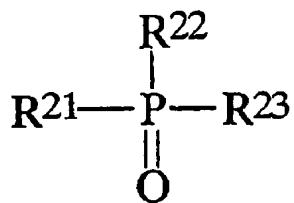
[0096]

In the invention, particularly preferable as the hydrogen bonding compound is the compound expressed by formula (D) shown below.

[0097]

Formula (D)

[Formula 13]



[0098]

In formula (D), R^{21} to R^{23} each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, or a heterocyclic group, which may be substituted or not substituted.

[0099]

In the case R^{21} to R^{23} contain a substituent, examples of the substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamido group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group, and the like, in which preferred as the substituents are an alkyl group or an aryl group, e.g., methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, a 4-alkoxyphenyl group, a 4-acyloxyphenyl group, and the like.

[0100]

Specific examples of an alkyl group expressed by R²¹ to R²³ include methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenetyl group, 2-phenoxypropyl group, and the like.

[0101]

As aryl groups, there can be mentioned phenyl group, cresyl group, xylyl group, naphthyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group, 3,5-dichlorophenyl group, and the like.

[0102]

As alkoxy groups, there can be mentioned methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group, benzyloxy group, and the like.

[0103]

As aryloxy groups, there can be mentioned phenoxy group, cresyloxy group, isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group, biphenyloxy group, and the like.

[0104]

As amino groups, there can be mentioned are dimethylamino group, diethylamino group, dibutylamino group, dioctylamino group, N-methyl-N-

hexylamino group, dicyclohexylamino group, diphenylamino group, N-methyl-N-phenylamino, and the like.

[0105]

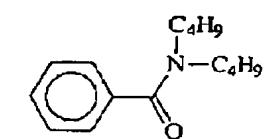
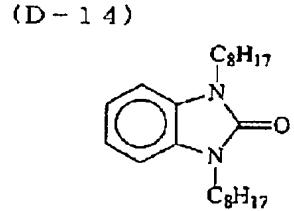
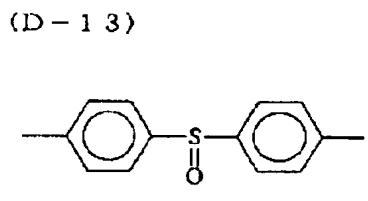
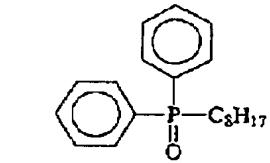
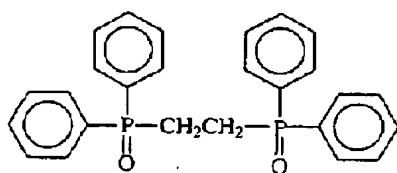
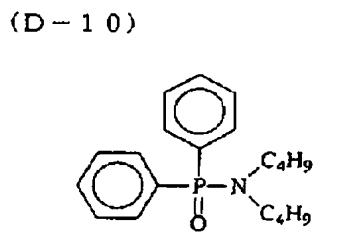
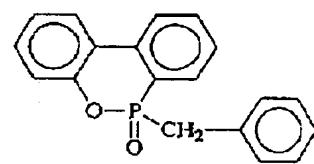
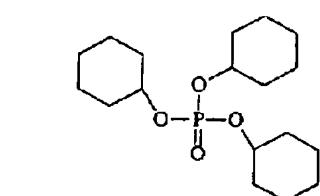
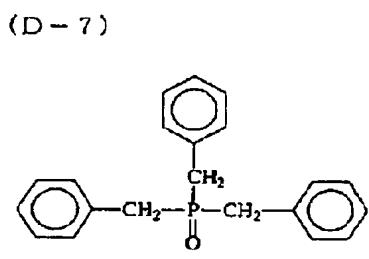
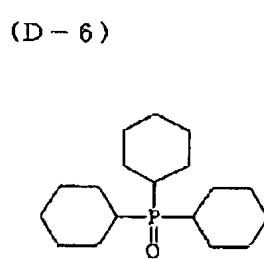
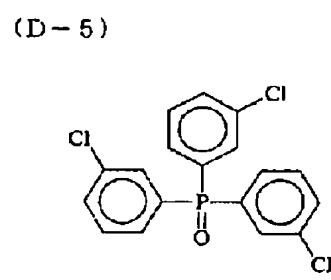
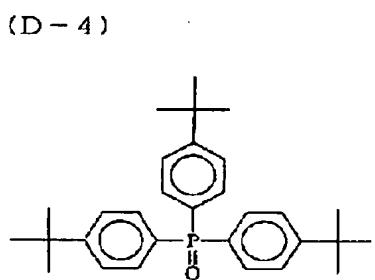
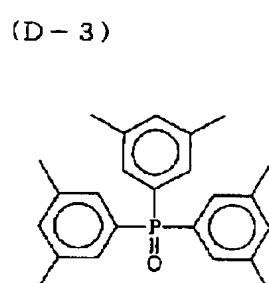
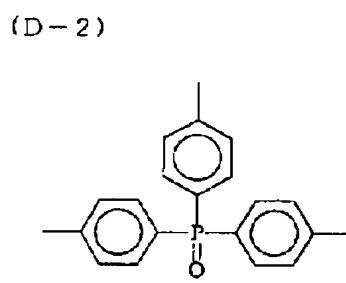
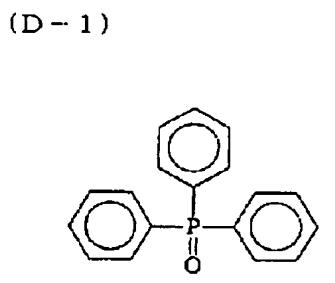
Preferred as R²¹ to R²³ are an alkyl group, an aryl group, an alkoxy group, and an aryloxy group. Concerning the effect of the invention, it is preferred that at least one or more of R²¹ to R²³ are an alkyl group or an aryl group, and more preferably, two or more of them are an alkyl group or an aryl group. From the viewpoint of low cost availability, it is preferred that R²¹ to R²³ are of the same group.

[0106]

Specific examples of hydrogen bonding compounds represented by formula (D) of the invention and others are shown below, but it should be understood that the invention is not limited thereto.

[0107]

[Formula 14]



[0108]

Specific examples of hydrogen bonding compounds other than those enumerated above can be found in those described in EP-A No. 1096310 and in JP-A No. 2002-156727 and Japanese Patent Application No. 2001-124796.

[0109]

The compound expressed by formula (D) used in the invention can be used in the photosensitive material by being incorporated into the coating solution in the form of solution, emulsion dispersion, or solid-dispersed fine particle dispersion similar to the case of reducing agent, however, it is preferred to be used after it is prepared in the form of solid-dispersed fine particle dispersion. In the solution, the compound expressed by formula (D) forms a hydrogen-bonded complex with a compound having a phenolic hydroxyl group or an amino group, and can be isolated as a complex in crystalline state depending on the combination of the reducing agent and the compound expressed by formula (D).

[0110]

It is particularly preferred to use the crystal powder thus isolated in the form of a solution by dissolving it into a coating solvent, because it provides stable performance. Further, it is also preferred to use a method of leading to form complex during dispersion by mixing the reducing agent and the compound expressed by formula (D) in the form of powders and dispersing them with a proper dispersion solvent using sand grinder mill and the like.

[0111]

The compound expressed by formula (D) is preferably used in the range of from 1 mol% to 200 mol%, more preferably from 10 mol% to 150 mol%, and further preferably, from 20 mol% to 100 mol%, with respect to the reducing agent.

[0112]

1.6. Silver halide

1) Halogen composition

For the photosensitive silver halide used in the invention, there is no particular restriction on the halogen composition and silver chloride, silver bromochloride, silver bromide, silver iodobromide, silver iodochlorobromide and silver iodide can be used. Among them, silver bromide, silver iodobromide and silver iodide are preferred. The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a silver halide grain having a core/shell structure can be used preferably. Preferred structure is a twofold to fivefold structure and, more preferably, core/shell grain having a twofold to fourfold structure can be used. Further, a technique of localizing silver bromide or silver iodide to the surface of a silver chloride, silver bromide or silver chlorobromide grains can also be used preferably.

[0113]

2) Method of grain formation

The method of forming photosensitive silver halide is well-known in the relevant art and, for example, methods described in Research Disclosure No.

10729, June 1978 and USP No. 3700458 can be used. Specifically, a method of preparing a photosensitive silver halide by adding a silver-supplying compound and a halogen-supplying compound in a gelatin or other polymer solution and then mixing them with an organic silver salt is used. Further, a method described in JP-A No. 11-119374 (paragraph Nos. 0217 to 0224) and methods described in JP-A Nos. 11-352627 and 2000-347335 are also preferred.

[0114]

3) Grain size

The grain size of the photosensitive silver halide is preferably small with an aim of suppressing clouding after image formation and, specifically, it is 0.20 μm or less, more preferably, 0.01 μm to 0.15 μm and, further preferably, 0.02 μm to 0.12 μm . The grain size as used herein means an average diameter of a circle converted such that it has a same area as a projection area of the silver halide grain (projection area of a main plane in a case of a tabular grain).

[0115]

4) Grain shape

The shape of the silver halide grain can include, for example, cubic, octahedral, plate-like, spherical, rod-like or potato-like shape. The cubic grain is particularly preferred in the invention. A silver halide grain rounded at corners can also be used preferably. While there is no particular restriction on the index of plane (Mirror's index) of an crystal surface of the photosensitive silver halide grain, it is preferred that the ratio of [100] face is higher, in which the spectral sensitizing efficiency is higher in a case of adsorption of a spectral sensitizing dye.

The ratio is preferably 50% or more, more preferably, 65% or more and, further preferably, 80% or more. The ratio of the Mirror's index [100] face can be determined by the method of utilizing the adsorption dependency of [111] face and [100] face upon adsorption of a sensitizing dye described by T. Tani; in *J. Imaging Sci.*, 29, 165 (1985).

[0116]

5) Heavy metal

The photosensitive silver halide grain of the invention can contain metals or complexes of metals belonging to groups 8 to 10 of the periodic table (showing groups 1 to 18). The metal or the center metal of the metal complex from groups 8 to 10 of the periodic table is preferably rhodium, ruthenium or iridium. The metal complex may be used alone, or two or more kinds of complexes comprising identical or different species of metals may be used together. A preferred content is in the range from 1×10^{-9} mol to 1×10^{-3} mol per one mol of silver. The heavy metals, metal complexes and the addition method thereof are described in JP-A No. 7-225449, in paragraph Nos. 0018 to 0024 of JP-A No. 11-65021 and in paragraph Nos. 0227 to 0240 of JP-A No. 11-119374.

[0117]

In the present invention, a silver halide grain having a hexacyano metal complex is present on the outermost surface of the grain is preferred. The hexacyano metal complex includes, for example, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Os}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CN})_6]^{3-}$, $[\text{Ir}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{3-}$, and $[\text{Re}(\text{CN})_6]^{3-}$. In the invention, hexacyano Fe complex is preferred.

[0118]

Since the hexacyano complex exists in ionic form in an aqueous solution, paired cation is not important and alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ion, alkyl ammonium ion (for example, tetramethyl ammonium ion, tetraethyl ammonium ion, tetrapropyl ammonium ion, and tetra(n-butyl) ammonium ion), which are easily miscible with water and suitable to precipitation operation of a silver halide emulsion are preferably used.

[0119]

The hexacyano metal complex can be added while being mixed with water, as well as a mixed solvent of water and an appropriate organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters and amides) or gelatin.

[0120]

The addition amount of the hexacyano metal complex is preferably from 1×10^{-5} mol to 1×10^{-2} mol and, more preferably, from 1×10^{-4} mol to 1×10^{-3} per one mol of silver in each case.

[0121]

In order to allow the hexacyano metal complex to be present on the outermost surface of a silver halide grain, the hexacyano metal complex is directly added in any stage of: after completion of addition of an aqueous solution

of silver nitrate used for grain formation, before completion of emulsion forming step prior to a chemical sensitization step, of conducting chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization or noble metal sensitization such as gold sensitization, during washing step, during dispersion step and before chemical sensitization step. In order not to grow the fine silver halide grain, the hexacyano metal complex is rapidly added preferably after the grain is formed, and it is preferably added before completion of the emulsion forming step.

[0122]

Addition of the hexacyano complex may be started after addition of 96% by mass of an entire amount of silver nitrate to be added for grain formation, more preferably started after addition of 98% by mass and, particularly preferably, started after addition of 99% by mass.

[0123]

When any of the hexacyano metal complex is added after addition of an aqueous silver nitrate just before completion of grain formation, it can be adsorbed to the outermost surface of the silver halide grain and most of them form an insoluble salt with silver ions on the surface of the grain. Since the hexacyano iron (II) silver salt is a less soluble salt than AgI, re-dissolution with fine grains can be prevented and fine silver halide grains with smaller grain size can be prepared.

[0124]

Metal atoms that can be contained in the silver halide grain used in the invention (for example, $[\text{Fe}(\text{CN})_6]^{4-}$), desalting method of a silver halide emulsion and chemical sensitization method are described in paragraph Nos. 0046 to 0050 of JP-A No. 11-84574, in paragraph Nos. 0025 to 0031 of JP-A No. 11-65021, and paragraph Nos. 0242 to 0250 of JP-A No. 11-119374.

[0125]

6) Gelatin

As the gelatin contained the photosensitive silver halide emulsion used in the invention, various kinds of gelatins can be used. It is necessary to maintain an excellent dispersion state of a photosensitive silver halide emulsion in an organic silver salt containing coating solution, and gelatin having a molecular weight of 10,000 to 1,000,000 is preferably used. And phthalated gelatin is also preferably used. These gelatins may be used at grain formation step or at the time of dispersion after desalting treatment and it is preferably used at grain formation step.

[0126]

7) Sensitizing dye

As the sensitizing dye applicable in the invention, those capable of spectrally sensitizing silver halide grains in a desired wavelength region upon adsorption to silver halide grains having spectral sensitivity suitable to spectral characteristic of an exposure light source can be selected advantageously. The sensitizing dyes and the addition method are disclosed, for example, JP-A No. 11-65021 (paragraph Nos. 0103 to 0109), as a compound represented by the formula

(II) in JP-A No. 10-186572, dyes represented by the formula (I) in JP-A No. 11-119374 (paragraph No. 0106), dyes described in USP Nos. 5510236 and 3871887 (Example 5), dyes disclosed in JP-A Nos. 2-96131 and 59-48753, as well as in page 19, line 38 to page 20, line 35 of EP-A No. 0803764A1, and in JP-A Nos. 2001-272747, 2001-290238 and 2002-23306. The sensitizing dyes described above may be used alone or two or more of them may be used in combination. In the invention, sensitizing dye can be added preferably after desalting step and before coating step, and more preferably after desalting step and before the completion of chemical ripening.

[0127]

In the invention, the sensitizing dye may be added at any amount according to the property of photosensitivity and fogging, but it is preferably added from 10^{-6} mol to 1 mol, and more preferably, from 10^{-4} mol to 10^{-1} mol per one mol of silver in each case.

[0128]

The photothermographic material of the invention may also contain super sensitizers in order to improve spectral sensitizing effect. The super sensitizers usable in the invention can include those compounds described in EP-A No. 587,338, USP Nos. 3877943 and 4873184 and JP-A Nos. 5-341432, 11-109547, and 10-111543.

[0129]

8) Chemical sensitization

The photosensitive silver halide grain in the invention is preferably chemically sensitized by sulfur sensitization method, selenium sensitization method or tellurium sensitization method. As the compound used preferably for sulfur sensitization method, selenium sensitization method and tellurium sensitization method, known compounds, for example, compounds described in JP-A No. 7-128768 can be used. Particularly, tellurium sensitization is preferred in the invention and compounds described in the literature cited in paragraph No. 0030 in JP-A No. 11-65021 and compounds shown by formulae (II), (III), and (IV) in JP-A No. 5-313284 are more preferred.

[0130]

The photosensitive silver halide grain in the invention is preferably chemically sensitized by gold sensitization method alone or in combination with the chalcogen sensitization described above. As the gold sensitizer, those having an oxidation number of gold of either +1 or +3 are preferred and those gold compounds used usually as the gold sensitizer are preferred. As typical examples, chloroauric acid, bromoauric acid, potassium chloroaurate, potassium bromoaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyl trichloro gold are preferred. Further, gold sensitizers described in USP No. 5858637 and Japanese Patent Application No. 2001-79450 are also used preferably.

[0131]

In the invention, chemical sensitization can be applied at any time so long

as it is after grain formation and before coating and it can be applied, after desalting, (1) before spectral sensitization, (2) simultaneously with spectral sensitization, (3) after spectral sensitization and (4) just before coating.

[0132]

The amount of sulfur, selenium and tellurium sensitizer used in the invention may vary depending on the silver halide grain used, the chemical ripening condition and the like and it is used by about 10^{-8} mol to 10^{-2} mol, preferably, 10^{-7} mol to 10^{-3} mol per one mol of the silver halide.

[0133]

The addition amount of the gold sensitizer may vary depending on various conditions and it is generally about 10^{-7} mol to 10^{-3} mol and, more preferably, 10^{-6} mol to 5×10^{-4} mol per one mol of the silver halide.

There is no particular restriction on the condition for the chemical sensitization in the invention and, appropriately, pH is 5 to 8, pAg is 6 to 11 and temperature is at 40°C to 95°C.

[0134]

In the silver halide emulsion used in the invention, a thiosulfonic acid compound may be added by the method shown in EP-A No. 293917.

[0135]

A reductive compound is used preferably for the photosensitive silver halide grain in the invention. As the specific compound for the reduction

sensitization, ascorbic acid or thiourea dioxide is preferred, as well as use of stannous chloride, aminoimino methane sulfonic acid, hydrazine derivatives, borane compounds, silane compounds and polyamine compounds are preferred. The reduction sensitizer may be added at any stage in the photosensitive emulsion production process from crystal growth to the preparation step just before coating. Further, it is preferred to apply reduction sensitization by ripening while keeping pH to 7 or higher or pAg to 8.3 or lower for the emulsion, and it is also preferred to apply reduction sensitization by introducing a single addition portion of silver ions during grain formation.

[0136]

9) Compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons

The photothermographic material of the invention preferably contains a compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons. The said compound can be used in combination with various chemical sensitizers described above to increase the sensitivity of silver halide.

[0137]

As the compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons is a compound selected from the following Groups 1 to 5.

[0138]

(Group 1) a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases at least two electrons, due to being subjected to a subsequent bond cleavage reaction;

[0139]

(Group 2) a compound that has at least two groups adsorptive to the silver halide and can be one-electron-oxidized to provide a one-electron oxidation product which further releases one electron, due to being subjected to a subsequent bond cleavage reaction;

[0140]

(Group 3) a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which further releases at least one electron after being subjected to a subsequent bond formation;

[0141]

(Group 4) a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases at least one electron after a subsequent intramolecular ring cleavage reaction; and

[0142]

(Group 5) a compound represented by X-Y, in which X represents a reducible group and Y represents a leaving group, and convertable by one-electron-oxidizing the reducible group to a one-electron oxidation product which can be converted into an X radical by eliminating the leaving group in a subsequent X-Y

bond cleavage reaction, one electron being released from the X radical.

[0143]

Each compound of Group 1 and Groups 3 to 5 preferably is a "compound having a sensitizing dye moiety" or a "compound having an adsorptive group to the silver halide". More preferred is a "compound having an adsorptive group to the silver halide". Each compound of Groups 1 to 4 more preferably is a "compound having a heterocyclic group containing nitrogen atoms substituted by two or more mercapto groups".

[0144]

The compound of Groups 1 to 5 will be described in detail below.

In the compound of Group 1, the term "the bond cleavage reaction" specifically means a cleavage reaction of a bond of carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin or carbon-germanium. Cleavage of a carbon-hydrogen bond may be followed after the cleavage reaction. The compound of Group 1 can be one-electron-oxidized to be converted into the one-electron oxidation product, and thereafter can release further two or more electrons, preferably three or more electrons with the bond cleavage reaction.

[0145]

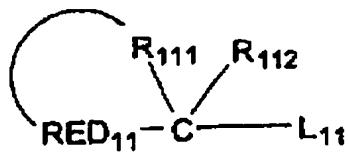
The compound of Group 1 is preferably represented by any one of formulae (A), (B), (1), (2) and (3).

[0146]

Formula (A)

[Formula 15]

Formula (A)

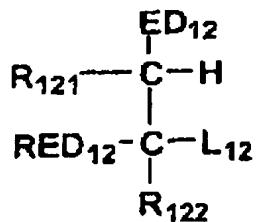


[0147]

Formula (B)

[Formula 16]

Formula (B)



[0148]

In formula (A), RED_{11} represents a reducible group that can be one-electron-oxidized, and L_{11} represents a leaving group. R_{112} represents a hydrogen atom or a substituent. R_{111} represents a nonmetallic atomic group forming a tetrahydro-, hexahydro- or octahydro-derivative of a 5- or 6-membered aromatic ring including aromatic heterocycles.

[0149]

In formula (B), RED_{12} represents a reducible group that can be one-

electron-oxidized, and L_{12} represents a leaving group. R_{121} and R_{122} each represent a hydrogen atom or a substituent. ED_{12} represents an electron-donating group. In formula (B), R_{121} and RED_{12} , R_{121} and R_{122} , and ED_{12} and RED_{12} may bond together to form a ring structure, respectively.

[0150]

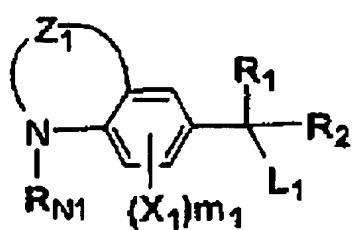
In the compound represented by formula (A) or (B), the reducible group of RED_{11} or RED_{12} is one-electron-oxidized, and thereafter the leaving group of L_{11} or L_{12} is spontaneously eliminated in the bond cleavage reaction. Further two or more, preferably three or more electrons can be released with the bond cleavage reaction.

[0151]

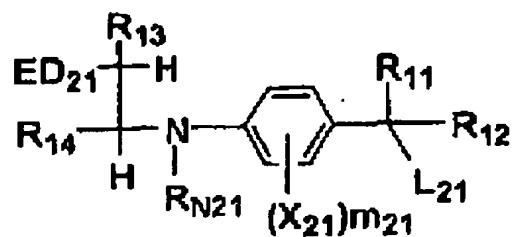
Formulae (1), (2) and (3)

[Formula 17]

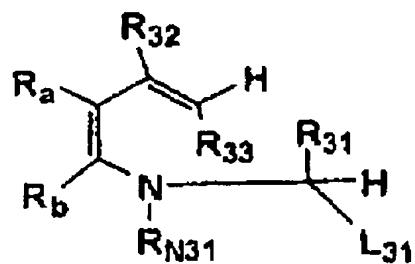
Formula (1)



Formula (2)



Formula (3)



[0152]

In formula (1), Z_1 represents an atomic group forming a 6-membered ring with a nitrogen atom and 2 carbon atoms in a benzene ring; R_1 , R_2 and R_{N1} each represent a hydrogen atom or a substituent; X_1 represents a substituent capable of substituting for a hydrogen atom on a benzene ring; m_1 represents an integer from 0 to 3; and L_1 represents a leaving group. In formula (2), ED_{21} represents an electron-donating group; R_{11} , R_{12} , R_{N21} , R_{13} and R_{14} each represent a hydrogen atom or a substituent; X_{21} represents a substituent capable of substituting for a hydrogen atom on a benzene ring; m_{21} represents an integer from 0 to 3; and L_{21} represents a leaving group. R_{N21} , R_{13} , R_{14} , X_{21} and ED_{21} may bond to each other to form a ring structure. In formula (3), R_{32} , R_{33} , R_{31} , R_{N31} , R_a and R_b each represent a hydrogen atom or a substituent; and L_{31} represents a leaving group. Incidentally, R_a and R_b bond together to form an aromatic ring when R_{N31} is not an aryl group.

[0153]

After the compound is one-electron-oxidized, the leaving group of L_1 , L_{21} or L_{31} is spontaneously eliminated in the bond cleavage reaction. Further two or more, preferably three or more electrons can be released with the bond cleavage reaction.

[0154]

First, the compound represented by formula (A) will be described in detail below.

In formula (A), the reducible group of RED_{11} can be one-electron-oxidized

and can bond to after-mentioned R_{111} to form the particular ring structure. Specifically, the reducible group may be a divalent group provided by removing one hydrogen atom from the following monovalent group at a position suitable for ring formation.

The monovalent group may be an alkylamino group; an arylamino group such as an anilino group and a naphthylamino group; a heterocyclic amino group such as a benzthiazolylamino group and a pyrrolylamino group; an alkylthio group; an arylthio group such as a phenylthio group; a heterocyclic thio group; an alkoxy group; an aryloxy group such as a phenoxy group; a heterocyclic oxy group; an aryl group such as a phenyl group, a naphthyl group and an anthranil group; or an aromatic or nonaromatic heterocyclic group, containing at least one heteroatom selected from the group consisting of a nitrogen atom, a sulfur atom, an oxygen atom and a selenium atom, which has a 5- to 7-membered, monocyclic or condensed ring structure such as a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinoxaline ring, a tetrahydroquinazoline ring, an indoline ring, an indole ring, an indazole ring, a carbazole ring, a phenoxazine ring, a phenothiazine ring, a benzothiazoline ring, a pyrrole ring, an imidazole ring, a thiazoline ring, a piperidine ring, a pyrrolidine ring, a morpholine ring, a benzimidazole ring, a benzimidazoline ring, a benzoxazoline ring and a methylenedioxyphenyl ring. (RED₁₁ is hereinafter described as the monovalent group for convenience.) The monovalent groups may have a substituent.

[0155]

Examples of the substituent include halogen atoms; alkyl groups

including aralkyl groups, cycloalkyl groups, active methine groups, etc.; alkenyl groups; alkynyl groups; aryl groups; heterocyclic groups, which may bond at any position; heterocyclic groups containing a quaternary nitrogen atom such as a pyridinio group, an imidazolio group, a quinolinio group and an isoquinolinio group; acyl groups; alkoxycarbonyl groups; aryloxycarbonyl groups; carbamoyl groups; a carboxy group and salts thereof; sulfonylcarbamoyl groups; acylcarbamoyl groups; sulfamoylcarbamoyl groups; carbazoyl groups; oxaryl groups; oxamoyl groups; a cyano group; carbonimidoyl groups; thiocarbamoyl groups; a hydroxy group; alkoxy groups, which may contain a plurality of ethyleneoxy groups or propyleneoxy groups as a repetition unit; aryloxy groups; heterocyclic oxy groups; acyloxy groups; alkoxy or aryloxy carbonyloxy groups; carbamoyloxy groups; sulfonyloxy groups; amino groups; alkyl, aryl or heterocyclic amino groups; acylamino groups; sulfoneamide groups; ureide groups; thioureide groups; imide groups; alkoxy or aryloxy carbonylamino groups; sulfamoylamino groups; semicarbazide groups; thiosemicarbazide groups; hydrazino groups; ammonio groups; oxamoylamino groups; alkyl or aryl sulfonylureide groups; acylureide groups; acylsulfamoylamino groups; a nitro group; a mercapto group; alkyl, aryl or heterocyclic thio groups; alkyl or aryl sulfonyl groups; alkyl or aryl sulfinyl groups; a sulfo group and salts thereof; sulfamoyl groups; acylsulfamoyl groups; sulfonylsulfamoyl groups and salts thereof; groups containing a phosphoric amide or phosphate ester structure; etc. These substituents may be further substituted by these substituents.

[0156]

RED₁₁ is preferably an alkylamino group, an arylamino group, a

heterocyclic amino group, an aryl group, an aromatic heterocyclic group, or nonaromatic heterocyclic group. RED_{11} is more preferably an arylamino group (particularly an anilino group), or an aryl group (particularly a phenyl group). When RED_{11} has a substituent, preferred as a substituent include halogen atoms, alkyl groups, alkoxy groups, carbamoyl groups, sulfamoyl groups, acylamino groups, sulfoneamide groups.

[0157]

When RED_{11} is an aryl group, it is preferred that the aryl group has at least one "electron-donating group". The "electron-donating group" is a hydroxy group; an alkoxy group; a mercapto group; a sulfoneamide group; an acylamino group; an alkylamino group; an arylamino group; a heterocyclic amino group; an active methine group; an electron-excess, aromatic, heterocyclic group with a 5-membered monocyclic ring or a condensed-ring including at least one nitrogen atom in the ring such as an indolyl group, a pyrrolyl group, an imidazolyl group, a benzimidazolyl group, a thiazolyl group, a benzthiazolyl group and an indazolyl group; a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom, such as so-called cyclic amino group like pyrrolidinyl group, an indolinyl group, a piperidinyl group, a piperazinyl group and a morpholino group; etc. The active methine group is a methine group having two "electron-attracting groups", and the "electron-attracting group" is an acyl group, an alkoxy carbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group or a carbonimidoyl group. The two electron-attracting groups may bond together to form a ring structure.

[0158]

In formula (A), specific examples of L_{11} include a carboxy group and salts thereof, silyl groups, a hydrogen atom, triarylboron anions, trialkylstannyly groups, trialkylgermyl groups and a $\cdot CR_{C1}R_{C2}R_{C3}$ group. When L_{11} represents a silyl group, the silyl group is specifically a trialkylsilyl group, an arylalkylsilyl group, a triarylsilyl group, etc, and they may have a substituent.

[0159]

When L_{11} represents a salt of a carboxy group, specific examples of a counter ion to form the salt include alkaline metal ions, alkaline earth metal ions, heavy metal ions, ammonium ions, phosphonium ions, etc. Preferred as a counter ion are alkaline metal ions and ammonium ions, most preferred are alkaline metal ions such as Li^+ , Na^+ and K^+ .

[0160]

When L_{11} represents a $\cdot CR_{C1}R_{C2}R_{C3}$ group, R_{C1} , R_{C2} and R_{C3} independently represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocyclic amino group, an alkoxy group, an aryloxy group or a hydroxy group. R_{C1} , R_{C2} and R_{C3} may bond to each other to form a ring structure, and may have a substituent. Incidentally, when one of R_{C1} , R_{C2} and R_{C3} is a hydrogen atom or an alkyl group, there is no case where the other two of them are a hydrogen atom or an alkyl group. R_{C1} , R_{C2} and R_{C3} are preferably an alkyl group, an aryl group (particularly a phenyl group), an

alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocyclic group, an alkoxy group or a hydroxy group, respectively. Specific examples thereof include a phenyl group, a *p*-dimethylaminophenyl group, a *p*-methoxyphenyl group, a 2,4-dimethoxyphenyl group, a *p*-hydroxyphenyl group, a methylthio group, a phenylthio group, a phenoxy group, a methoxy group, an ethoxy group, a dimethylamino group, an *N*-methylanilino group, a diphenylamino group, a morpholino group, a thiomorpholino group, a hydroxy group, etc. Examples of the ring structure formed by R_{C1} , R_{C2} and R_{C3} include a 1,3-dithiolane-2-yl group, a 1,3-dithiane-2-yl group, an *N*-methyl-1,3-thiazolidine-2-yl group, an *N*-benzyl-benzothiazolidine-2-yl group, etc.

[0161]

It is also preferred that the $\text{-CR}_{C1}\text{R}_{C2}\text{R}_{C3}$ group is the same as a residue provided by removing L_{11} from formula (A) as a result of selecting each of R_{C1} , R_{C2} and R_{C3} as above.

[0162]

In formula (A), L_{11} is preferably a carboxy group or a salt thereof, or a hydrogen atom, more preferably a carboxy group or a salt thereof.

[0163]

When L_{11} represents a hydrogen atom, the compound represented by formula (A) preferably has a base moiety. After the compound represented by formula (A) is oxidized, the base moiety acts to eliminate the hydrogen atom of L_{11} and to release an electron.

[0164]

The base is specifically a conjugate base of an acid with a pKa value of approximately 1 to 10. For example, the base moiety may contain a structure of a nitrogen-containing heterocycle such as pyridine, imidazole, benzoimidazole and thiazole; aniline; trialkylamine; an amino group; a carbon acid such as an active methylene anion; a thioacetic acid anion; carboxylate (-COO^-); sulfate (-SO_3^-); amineoxide ($\text{>N}^+(\text{O}^-)\text{-}$); and derivatives thereof. The base is preferably a conjugate base of an acid with a pKa value of approximately 1 to 8, more preferably carboxylate, sulfate or amineoxide, particularly preferably carboxylate. When these bases have an anion, the compound of formula (A) may have a counter cation. Examples of the counter cation include alkaline metal ions, alkaline earth metal ions, heavy metal ions, ammonium ions, phosphonium ions, etc. The base moiety may be at an optional position of the compound represented by formula (A). The base moiety may be connected to RED_{11} , R_{111} or R_{112} in formula (A), and to a substituent thereon.

[0165]

In formula (A), R_{112} represents a substituent capable of substituting a hydrogen atom or a carbon atom therewith, provided that R_{112} and L_{11} do not represent the same group.

[0166]

R_{112} preferably represents a hydrogen atom, an alkyl group, an aryl group (such as a phenyl group), an alkoxy group (such as a methoxy group, a ethoxy

group, a benzyloxy group), a hydroxy group, an alkylthio group, (such as a methylthio group, a butylthio group), and amino group, an alkylamino group, an arylamino group, a heterocyclic amino group or the like; and more preferably represents a hydrogen atom, an alkyl group, an alkoxy group, a hydroxy group, a phenyl group and an alkylamino group.

[0167]

Ring structures formed by R_{111} in formula (A) are ring structures corresponding to a tetrahydro structure, a hexahydro structure, or an octahydro structure of a five-membered or six-membered aromatic ring (including an aromatic hetero ring), wherein a hydro structure means a ring structure in which partial hydrogenation is performed on a carbon-carbon double bond (or a carbon-nitrogen double bond) contained in an aromatic ring (an aromatic hetero ring) as a part thereof, wherein the tetrahydro structure is a structure in which 2 carbon-carbon double bonds (or carbon-nitrogen double bonds) are hydrogenated, the hexahydro structure is a structure in which 3 carbon-carbon double bonds (or carbon-nitrogen double bonds) are hydrogenated, and the octahydro structure is a structure in which 4 carbon-carbon double bonds (or carbon-nitrogen double bonds) are hydrogenated. Hydrogenation of an aromatic ring produces a partially hydrogenated non-aromatic ring structure.

[0168]

Examples include a pyrrolidine ring, an imidazolidine ring, a thiazolidine ring, a pyrazolidine ring, an oxazolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a

tetralin ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring and a tetrahydroquinoxaline ring, a tetrahydrocarbazole ring, an octahydrophenanthridine ring and the like. The ring structures may have a substituent therein.

[0169]

More preferable examples of a ring structure forming R_{111} include a pyrrolidine ring, an imidazolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring, a tetrahydroquinoxaline ring and a tetracarbazole ring. Particularly preferable examples include a pyrrolidine ring, a piperidine ring, a piperazine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring and a tetrahydroquinoxaline ring; and most preferable examples include a pyrrolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring and a tetrahydroisoquinoline ring.

[0170]

In formula (B), RED_{12} and L_{12} represent groups having the respective same meanings as RED_{11} and L_{11} in formula (A), and have the respective same preferable ranges as RED_{11} and L_{11} in formula (A). RED_{12} is a monovalent group except a case where RED_{12} forms the following ring structure and to be concrete, there are exemplified groups each with a name of a monovalent group described as RED_{11} . RED_{121} and L_{122} represent groups having the same

meaning as R_{112} in formula (A), and have the same preferable range as R_{112} in formula (A). ED_{12} represents an electron-donating group. Each pair of R_{121} and RED_{12} ; R_{121} and R_{122} ; or ED_{12} and RED_{12} may form a ring structure by bonding with each other.

[0171]

An electron-donating group represented by RED_{12} in formula (B) is the same as an electron-donating group described as a substituent when RED_{11} represents an aryl group. Preferable examples of RED_{12} include a hydroxy group, an alkoxy group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, an electron-excessive aromatic heterocyclic group in a five-membered single ring or fused ring structure containing at least one nitrogen atom in a ring structure as part of the ring, a non-aromatic nitrogen containing heterocyclic group having a nitrogen atom as a substitute, and a phenyl group substituted with an electron donating group described above, and more preferable examples thereof include a non-aromatic nitrogen containing heterocyclic group further substituted with a hydroxy group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, or a nitrogen atom; and a phenyl group substituted with an electron-donating group described above (for example, a p-hydroxyphenyl group, a p-dialkylaminophenyl group, an o- or p-dialkoxyphenyl group and the like).

[0172]

In formula (B), R_{121} and RED_{12} ; R_{122} and R_{121} ; or ED_{12} and RED_{12} may

bond to each other to form a ring structure. A ring structure formed here is a non-aromatic carbon ring or hetero ring in a 5- to 7-membered single ring or fused ring structure which is substituted or unsubstituted. Concrete examples of a ring structure formed from R_{121} and RED_{12} include, in addition to the examples of the ring structure formed by R_{111} in formula (A), a pyrroline ring, an imidazoline ring, a thiazoline ring, a pyrazoline ring, an oxazoline ring, an indan ring, a morphorine ring, an indoline ring, a tetrahydro-1,4-oxazine ring, 2,3-dihydrobenzo-1,4-oxazine ring, a tetrahydro-1,4-thiazine ring, 2,3-dihydrobenzo-1,4-thiazine ring, 2,3-dihydrobenzofuran ring, 2,3-dihydrobenzothiophene ring and the like. In formation of a ring structure from ED_{12} and RED_{12} , ED_{12} is preferably an amino group, an alkylamino group or an arylamino group and concrete examples of the ring structure include a tetrahydropyrazine ring, a piperazine ring, a tetrahydroquinoxaline ring, a tetrahydroisoquinoline ring and the like. Concrete examples of a ring structure formed from R_{122} and R_{121} include a cyclohexane ring, a cyclopentane ring and the like.

[0173]

Below, description will be given of formulae (1) to (3).

In formulae (1) to (3), R_1 , R_2 , R_{11} , R_{12} and R_{31} represent the same meaning as R_{112} of formula (A) and have the same preferable range as R_{112} of formula (A). L_1 , L_{21} and L_{31} independently represents the same leaving groups as the groups shown as concrete examples in description of L_{11} of formula (A) and also have the same preferable range as L_{11} of formula (A). The substituents represented by X_1 and X_{21} are the same as the examples of substituents of RED_{11} of formula (A) and have the same preferable range as RED_{11} of formula (A). m_1 and m_2 are

preferably integers from 0 to 2 and more preferably integer of 0 or 1.

[0174]

When R_{N1} , R_{N21} and R_{N31} each represent a substituent, preferred as a substituent include an alkyl group, an aryl group or a heterocyclic group, and may further have a substituent. Each of R_{N1} , R_{N21} and R_{N31} is preferably a hydrogen atom, an alkyl group or an aryl group, more preferably a hydrogen atom or an alkyl group.

[0175]

When R_{13} , R_{14} , R_{32} , R_{33} , R_a and R_b independently represent a substituent, the substituent is preferably an alkyl group, an aryl group, an acyl group, an alkoxy carbonyl group, a carbamoyl group, a cyano group, an alkoxy group, an acylamino group, a sulfoneamide group, a ureide group, a thiouredide group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, or a sulfamoyl group.

[0176]

The 6-membered ring formed by Z_1 in formula (1) is a nonaromatic heterocycle condensed with the benzene ring in formula (1). The ring structure containing the nonaromatic heterocycle and the benzene ring to be condensed may be specifically a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, or a tetrahydroquinazoline ring, which may have a substituent.

[0177]

In formula (2), ED_{21} is the same as ED_{12} in formula (B) with respect to the meanings and preferred embodiments.

[0178]

In formula (2), any two of RN_{21} , R_{13} , R_{14} , X_{21} and ED_{21} may bond together to form a ring structure. The ring structure formed by R_{N21} and X_{21} is preferably a 5- to 7-membered, carbocyclic or heterocyclic, nonaromatic ring structure condensed with a benzene ring, and specific examples thereof include a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, an indoline ring, a 2,3-dihydro-5,6-benzo-1,4-thiazine ring, etc. Preferred are a tetrahydroquinoline ring, a tetrahydroquinoxaline ring and an indoline ring.

[0179]

When R_{N31} is a group other than an aryl group in formula (3), R_a and R_b bond together to form an aromatic ring. The aromatic ring is an aryl group such as a phenyl group and a naphthyl group, or an aromatic heterocyclic group such as a pyridine ring group, a pyrrole ring group, a quinoline ring group and an indole ring group, preferably an aryl group. The aromatic ring group may have a substituent.

[0180]

In formula (3), R_a and R_b preferably bond together to form an aromatic ring, particularly a phenyl group.

[0181]

In formula (3), R₃₂ is preferably a hydrogen atom, an alkyl group, an aryl group, a hydroxy group, an alkoxy group, a mercapto group or an amino group.

When R₃₂ is a hydroxy group, R₃₃ is preferably an electron-attracting group.

The electron-attracting group is the same as described above, preferably an acyl group, an alkoxy carbonyl group, a carbamoyl group or a cyano group.

[0182]

The compound of Group 2 will be described below.

According to the compound of Group 2, the "bond cleavage reaction" is a cleavage reaction of a bond of carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin or carbon-germanium. Cleavage of a carbon-hydrogen bond may be caused with the cleavage reaction.

[0183]

The compound of Group 2 has two or more, preferably 2 to 6, more preferably 2 to 4, adsorbent groups to the silver halide. The adsorptive group is further preferably a mercapto-substituted, nitrogen-containing, heterocyclic group. The adsorptive group will hereinafter be described.

[0184]

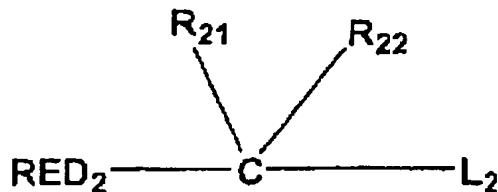
The compound of Group 2 is preferably represented by the following formula (C).

[0185]

Formula (C)

[Formula 18]

Formula (C)



[0186]

In the compound represented by formula (C), the reducible group of RED_2 is one-electron-oxidized, and thereafter the leaving group of L_2 is spontaneously eliminated, thus a C (carbon atom)- L_2 bond is cleaved, in the bond cleavage reaction. Further one electron can be released with the bond cleavage reaction.

[0187]

In formula (C), RED_2 is the same as RED_{12} in formula (B) with respect to the meanings and preferred embodiments. L_2 is the same as L_{11} in formula (A) with respect to the meanings and preferred embodiments. Incidentally, when L_2 is a silyl group, the compound of formula (C) has two or more mercapto-substituted, nitrogen-containing, heterocyclic groups as the adsorbent groups. R_{21} and R_{22} each represent a hydrogen atom or a substituent, and are the same as R_{112} in formula (A) with respect to the meanings and preferred embodiments. RED_2 and R_{21} may bond together to form a ring structure.

[0188]

The ring structure is a 5- to 7-membered, monocyclic or condensed, carbocyclic or heterocyclic, nonaromatic ring, and may have a substituent.

Incidentally, there is no case where the ring structure corresponds to a tetrahydro-, hexahydro- or octahydro-derivative of an aromatic ring or an aromatic heterocycle. The ring structure is preferably such that corresponds to a dihydro-derivative of an aromatic ring or an aromatic heterocycle, and specific examples thereof include a 2-pyrroline ring, a 2-imidazoline ring, a 2-thiazoline ring, a 1,2-dihydropyridine ring, a 1,4-dihydropyridine ring, an indoline ring, a benzoimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 2,3-dihydrobenzothiophene ring, a 2,3-dihydrobenzofuran ring, a benzo- α -pyran ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring, a 1,2-dihydroquinoxaline ring, etc. Preferred are a 2-imidazoline ring, a 2-thiazoline ring, an indoline ring, a benzoimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 1,2-dihydro pyridine ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring and a 1,2-dihydroquinoxaline ring, more preferred are an indoline ring, a benzoimidazoline ring, a benzothiazoline ring and a 1,2-dihydroquinoline ring, particularly preferred is an indoline ring.

[0189]

The compound of Group 3 will be described below.

According to the compound of Group 3, "bond formation" means that a bond of carbon-carbon, carbon-nitrogen, carbon-sulfur, carbon-oxygen, etc. is formed.

[0190]

It is preferable that the one-electron oxidation product releases one or more electrons after an intramolecular bond-forming reaction between the one-

electron-oxidized portion and a reactive site in the same molecular such as a carbon-carbon double bond, a carbon-carbon triple bond, an aromatic group and a benzo-condensed, nonaromatic heterocyclic group.

[0191]

To be more detailed, a one-electron oxidized product (a cation radical species or a neutral radical species generated by elimination of a proton therefrom) formed by one electron oxidizing a compound of Group 3 reacts with a reactive group described above coexisting in the same molecule to form a bond and form a radical species having a new ring structure therein. The radical species have a feature to release a second electron directly or in company with elimination of a proton therefrom.

One of compounds of Group 3 has a chance to further release one or more electrons, in a ordinary case two or more electrons, after formation of a two-electron oxidized product, after receiving a hydrolysis reaction in one case or after causing a tautomerization reaction accompanying direct migration of a proton in another case. Alternatively, compounds of Group 3 also include a compound having an ability to further release one or more electron, in an ordinary case two or more electrons directly from a two-electron oxidized product, not by way of a tautomerization reaction.

[0192]

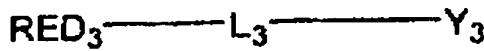
The compound of Group 3 is preferably represented by the following formula (D).

[0193]

Formula (D)

[Formula 19]

Formula (D)



[0194]

In formula (D), RED_3 represents a reducible group that can be one-electron-oxidized, and Y_3 represents a reactive group that reacts with the one-electron-oxidized RED_3 , specifically an organic group containing a carbon-carbon double bond, a carbon-carbon triple bond, an aromatic group or a benzo-condensed, nonaromatic heterocyclic group. L_3 represents a linking group that connects RED_3 and Y_3 .

[0195]

In formula (D), RED_3 has the same meanings as RED_{12} in formula (B). In formula (D), RED_3 is preferably an arylamino group, a heterocyclic amino group, an aryloxy group, an arylthio group, an aryl group, or an aromatic or nonaromatic heterocyclic group that is preferably a nitrogen-containing heterocyclic group. RED_3 is more preferably an arylamino group, a heterocyclic amino group, an aryl group, or an aromatic or nonaromatic heterocyclic group. Preferred as the heterocyclic group are a tetrahydroquinoline ring group, a tetrahydroquinoxaline ring group, a tetrahydroquinazoline ring group, an indoline ring group, an indole ring group, a carbazole ring group, a phenoxazine ring group, a phenothiazine ring group, a benzothiazoline ring group, a pyrrole

ring group, an imidazole ring group, a thiazole ring group, a benzoimidazole ring group, a benzoimidazoline ring group, a benzothiazoline ring group, a 3,4-methylenedioxyphenyl-1-yl group, etc.

[0196]

Particularly preferred as RED_3 are an arylamino group (particularly an anilino group), an aryl group (particularly a phenyl group), and an aromatic or nonaromatic heterocyclic group.

[0197]

The aryl group represented by RED_3 preferably has at least one electron-donating group. The term "electron-donating group" means the same as above-mentioned electron-donating group.

[0198]

When RED_3 is an aryl group, more preferred as a substituent on the aryl group are an alkylamino group, a hydroxy group, an alkoxy group, a mercapto group, a sulfoneamide group, an active methine group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom, furthermore preferred are an alkylamino group, a hydroxy group, an active methine group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom, and the most preferred are an alkylamino group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom.

[0199]

When Y_3 is an organic group containing carbon-carbon double bond (for example a vinyl group) having a substituent, more preferred as the substituent are an alkyl group, a phenyl group, an acyl group, a cyano group, an alkoxy carbonyl group, a carbamoyl group and an electron-donating group. The electron-donating group is preferably an alkoxy group; a hydroxy group (that may be protected by a silyl group, and examples of the silyl-protected group include a trimethylsilyloxy group, a *t*-butyldimethylsilyloxy group, a triphenylsilyloxy group, a triethylsilyloxy group, a phenyldimethylsilyloxy group, etc); an amino group; an alkylamino group; an arylamino group; a sulfoneamide group; an active methine group; a mercapto group; an alkylthio group; or a phenyl group having the electron-donating group as a substituent.

[0200]

Incidentally, when the organic group containing the carbon-carbon double bond has a hydroxy group as a substituent, Y_3 contains a moiety of $>C_1=C_2(-OH)-$, which may be tautomerized into a moiety of $>C_1H-C_2(=O)-$. In this case, it is preferred that a substituent on the C_1 carbon is an electron-attracting group, and as a result, Y_3 has a moiety of an active methylene group or an active methine group. The electron-attracting group, which can provide such a moiety of an "active methylene group" or an "active methine group", may be the same as above-mentioned electron-attracting group on the methine group of the "active methine group".

[0201]

When Y_3 is an organic group containing a carbon-carbon triple bond (for example a ethynyl group) having a substituent, preferred as the substituent is an alkyl group, a phenyl group, an alkoxy carbonyl group, a carbamoyl group, an electron-donating group, etc.

[0202]

When Y_3 is an organic group containing an aromatic group, preferable as the aromatic group is an aryl group, particularly a phenyl group, having an electron-donating group as a substituent, and an indole ring group. The electron-donating group is preferably a hydroxy group, which may be protected by a silyl group; an alkoxy group; an amino group; an alkylamino group; an active methine group; a sulfoneamide group; or a mercapto group.

[0203]

When Y_3 is an organic group containing a benzo-condensed, nonaromatic heterocyclic group, preferred as the benzo-condensed, nonaromatic heterocyclic group are groups having an aniline moiety, such as an indoline ring group, a 1,2,3,4-tetrahydroquinoline ring group, a 1,2,3,4-tetrahydroquinoxaline ring group and a 4-quinolone ring group.

[0204]

The reactive group of Y_3 is more preferably an organic group containing a carbon-carbon double bond, an aromatic group, or a benzo-condensed, nonaromatic heterocyclic group. Furthermore preferred are an organic group containing a carbon-carbon double bond; a phenyl group having an electron-

donating group as a substituent; an indole ring group; and a benzo-condensed, nonaromatic heterocyclic group having an aniline moiety. The carbon-carbon double bond more preferably has at least one electron-donating group as a substituent.

[0205]

It is also preferred that the reactive group represented by Y_3 contains a moiety the same as the reducible group represented by RED_3 as a result of selecting the reactive group as above.

[0206]

L_3 represents a linking group that connects RED_3 and Y_3 , specifically a single bond, an alkylene group, an arylene group, a heterocyclic group, $\cdot O\cdot$, $\cdot S\cdot$, $\cdot NR_N\cdot$, $\cdot C(=O)\cdot$, $\cdot SO_2\cdot$, $\cdot SO\cdot$, $\cdot P(=O)\cdot$, or a combination thereof. R_N represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. The linking group represented by L_3 may have a substituent. The linking group represented by L_3 may bond to each of RED_3 and Y_3 at an optional position such that the linking group substitutes optional one hydrogen atom of each RED_3 and Y_3 . Preferred examples of L_3 include a single bond; alkylene groups, particularly a methylene group, an ethylene group or a propylene group; arylene groups, particularly a phenylene group; a $\cdot C(=O)\cdot$ group; a $\cdot O\cdot$ group; a $\cdot NH\cdot$ group; $\cdot N(alkyl)\cdot$ groups; and divalent linking groups of combinations thereof.

[0207]

When a cation radical ($X^{+}\cdot$) provided by oxidizing RED_3 or a radical ($X\cdot$)

provided by eliminating a proton therefrom reacts with the reactive group represented by Y_3 to form a bond, it is preferable that they form a 3 to 7-membered ring structure containing the linking group represented by L_3 . Thus, the radical (X^+ or $X\cdot$) and the reactive group of Y are preferably connected through 3 to 7 atoms.

[0208]

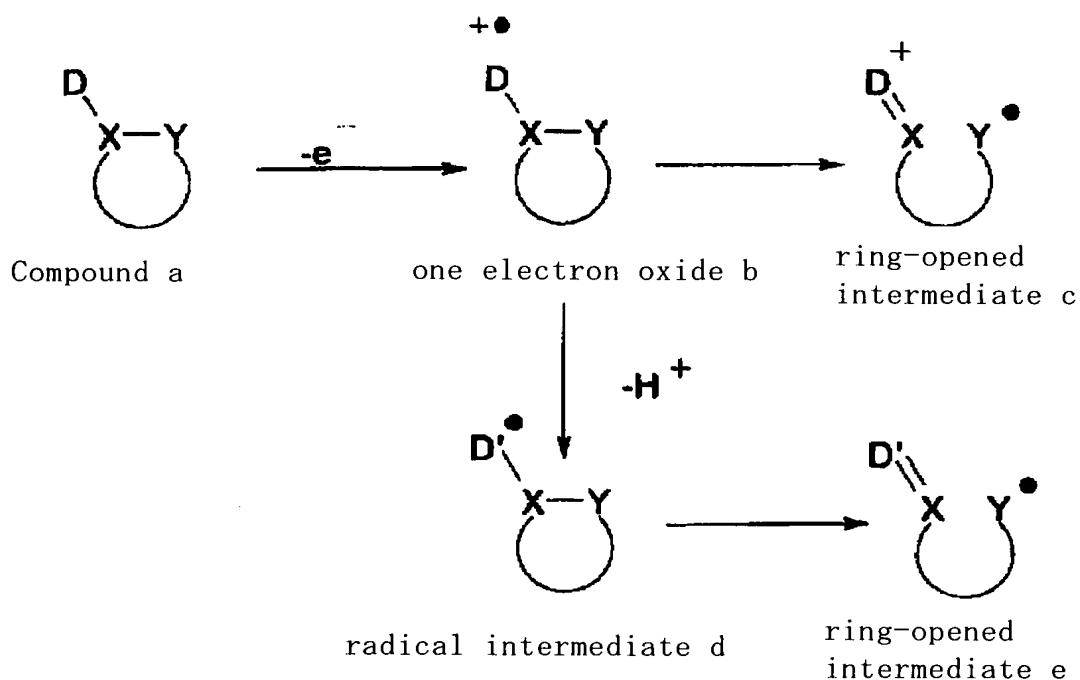
Next, the compound of Group 4 will be described below.

The compound of Group 4 has a reducible group-substituted ring structure. After the reducible group is one-electron-oxidized, the compound can release further one or more electrons with a ring structure cleavage reaction.

The ring cleavage reaction proceeds as follows.

[0209]

[Formula 20]



[0210]

In the formula, compound *a* is the compound of Group 4. In compound *a*, D represents a reducible group, and X and Y each represent an atom forming a bond in the ring structure, which is cleaved after the one-electron oxidation. First, compound *a* is one-electron-oxidized to generate one-electron oxidation product *b*. Then, the X-Y bond is cleaved with conversion of the D-X single bond into a double bond, whereby ring-opened intermediate *c* is provided. Alternatively, there is a case where one-electron oxidation product *b* is converted into radical intermediate *d* with deprotonation, and ring-opened intermediate *e* is provided in the same manner. Subsequently, further one or more electrons are released from thus-provided ring-opened intermediate *c* or *e*.

[0211]

The ring structure in the compound of Group 4 is a 3 to 7-membered,

carbocyclic or heterocyclic, monocyclic or condensed, saturated or unsaturated, nonaromatic ring. The ring structure is preferably a saturated ring structure, more preferably 3- or 4-membered ring. Preferred examples of the ring structure include a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring, an aziridine ring, an azetidine ring, an episulphide ring and a thietane ring. More preferred are a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring and an azetidine ring, particularly preferred are a cyclopropane ring, a cyclobutane ring and an azetidine ring. The ring structure may have a substituent.

[0212]

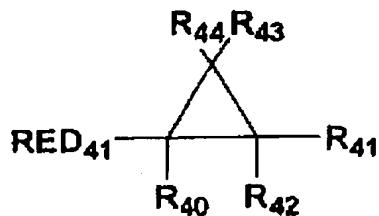
The compound of Group 4 is preferably represented by the following formulae (E) or (F).

[0213]

Formula (E)

[Formula 21]

Formula (E)

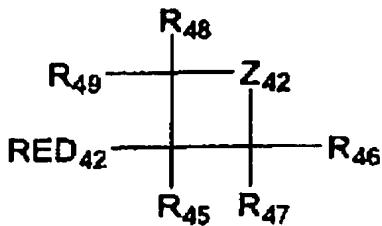


[0214]

Formula (F)

[Formula 22]

Formula (F)



[0215]

In formulae (E) and (F), RED_{41} and RED_{42} are the same as RED_{12} in formula (B) with respect to the meanings and preferred embodiments, respectively. R_{40} to R_{44} and R_{45} to R_{49} each represent a hydrogen atom or a substituent. In formula (F), Z_{42} represents $\cdot CR_{420}R_{421}\cdot$, $\cdot NR_{423}\cdot$, or $\cdot O\cdot$. R_{420} and R_{421} each represent a hydrogen atom or a substituent, and R_{423} represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

[0216]

In formulae (E) and (F), each of R_{40} and R_{45} is preferably a hydrogen atom, an alkyl group or an aryl group, more preferably a hydrogen atom, an alkyl group or an aryl group. Each of R_{41} to R_{44} and R_{46} to R_{49} is preferably a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, an arylthio group, an alkylthio group, an acylamino group or a sulfoneamide group, more preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group,

[0217]

It is preferred that at least one of R_{41} to R_{44} is a donor group, and it is also

preferred that both of R_{41} and R_{42} , or both of R_{43} and R_{44} are an electron-attracting group. It is more preferred that at least one of R_{41} to R_{44} is a donor group. It is furthermore preferred that at least one of R_{41} to R_{44} is a donor group and R_{41} to R_{44} other than the donor group are selected from a hydrogen atom and an alkyl group.

[0218]

A donor group referred to here is an “electron-donating group” or an aryl group substituted with at least one “electron-donating group.” Preferable examples of donor groups include an alkylamino group, an arylamino group, a heterocyclicamino group, an electron-excessive aromatic heterocyclic group in a five-membered single ring or fused ring structure containing at least one nitrogen atom in a ring structure as part of the ring, a non-aromatic nitrogen containing heterocyclic group having a nitrogen atom as a substitute and a phenyl group substituted with at least one electron-donating group. More preferable examples thereof include an alkylamino group, an aryamino group, an electron excessive aromatic heterocyclic group in a five-membered single ring or fused ring containing at least one nitrogen atom in a ring structure as a part (an indol ring, a pyrrole ring, a carbazole ring and the like), and a phenyl group substituted with an electron-donating group (a phenyl group substituted with three or more alkoxy groups, a phenyl group substituted with a hydroxy group, an alkylamino group, or an arylamino group and the like). Particularly preferable examples thereof include an aryamino group, an electron excessive aromatic heterocyclic group in a five-membered single ring or fused ring containing at least one nitrogen atom in a ring structure as a part (especially, a 3-

indolyl group), and a phenyl group substituted with an electron-donating group (especially, a trialkoxyphenyl group and a phenyl group substituted with an alkylamino group or an arylamino group).

[0219]

Z_{42} is preferably $\cdot CR_{420}R_{421}\cdot$ or $\cdot NR_{423}\cdot$, more preferably $\cdot NR_{423}\cdot$. Each of R_{420} and R_{421} is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an acylamino group or a sulfoneamino group, more preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. R_{423} is preferably a hydrogen atom, an alkyl group, an aryl group or an aromatic heterocyclic group, more preferably a hydrogen atom, an alkyl group or an aryl group.

[0220]

The substituent represented by each of R_{40} to R_{49} , R_{420} , R_{421} and R_{423} preferably has 40 or less carbon atoms, more preferably has 30 or less carbon atoms, particularly preferably 15 or less carbon atoms. The substituents of R_{40} to R_{49} , R_{420} , R_{421} and R_{423} may bond to each other or to the other portion such as RED_{41} , RED_{42} and Z_{42} , to form a ring.

[0221]

In the compounds of Groups 1 to 4 used in the invention, the adsorptive group to the silver halide is such a group that is directly adsorbed on the silver halide or promotes adsorption of the compound onto the silver halide. Specifically, the adsorptive group is a mercapto group or a salt thereof; a thione

group (-C(=S)-); a heterocyclic group containing at least one atom selected from the group consisting of a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom; a sulfide group; a cationic group; or an ethynyl group.

Incidentally, the adsorptive group in the compound of Group 2 is not a sulfide group.

[0222]

The mercapto group or a salt thereof used as the adsorptive group may be a mercapto group or a salt thereof itself, and is more preferably a heterocyclic group, an aryl group or an alkyl group having a mercapto group or a salt thereof as a substituent. The heterocyclic group is a 5- to 7-membered, monocyclic or condensed, aromatic or nonaromatic, heterocyclic group. Examples thereof include an imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzthiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, a triazine ring group, etc. The heterocyclic group may contain a quaternary nitrogen atom, and in this case, the mercapto group bonding to the heterocyclic group may be dissociated into a mesoion. Such heterocyclic group may be an imidazolium ring group, a pyrazolium ring group, a thiazolium ring group, a triazolium ring group, a tetrazolium ring group, a thiadiazolium ring group, a pyridinium ring group, a pyrimidinium ring group, a triazinium ring group, etc. Preferred among them is a triazolium ring group such as a 1,2,4-triazolium-3-thiolate ring group. Examples of the aryl group include a phenyl group and a naphthyl group.

Examples of the alkyl group include straight, branched or cyclic alkyl groups having 1 to 30 carbon atoms. When the mercapto group forms a salt, a counter ion of the salt may be a cation of an alkaline metal, an alkaline earth metal, a heavy metal, etc. such as Li^+ , Na^+ , K^+ , Mg^{2+} , Ag^+ and Zn^{2+} ; an ammonium ion; a heterocyclic group containing a quaternary nitrogen atom; a phosphonium ion; etc.

[0223]

Further, the mercapto group used as the adsorptive group may be tautomerized into a thione group. Specific examples of the thione group include a thioamide group (herein a $-\text{C}(=\text{S})\text{-NH-}$ group); and groups containing a structure of the thioamide group, such as linear or cyclic thioamide groups, a thiouredide group, a thiourethane group and a dithiocarbamic acid ester group. Examples of the cyclic thioamide group include a thiazolidine-2-thione group, an oxazolidine-2-thione group, a 2-thiohydantoin group, a rhodanine group, an isorhodanine group, a thiobarbituric acid group, a 2-thioxo-oxazolidine-4-one group, etc.

[0224]

The thione group used as the adsorbent group, as well as the thione group derived from the mercapto group by tautomerization, may be a linear or cyclic, thioamide, thiouredide, thiourethane or dithiocarbamic acid ester group that cannot be tautomerized into the mercapto group or has no hydrogen atom at α -position of the thione group.

[0225]

The heterocyclic group containing at least one atom selected from the group consisting of a nitrogen atom, a sulfur atom, a selenium atom and tellurium atom, which is used as the adsorbent group, is a nitrogen-containing heterocyclic group having a $\cdot\text{NH}\cdot$ group that can form a silver imide ($>\text{N}\text{Ag}$) as a moiety of the heterocycle; or a heterocyclic group having a $\cdot\text{S}\cdot$ group, a $\cdot\text{Se}\cdot$ group, a $\cdot\text{Te}\cdot$ group or a $=\text{N}\cdot$ group that can form a coordinate bond with a silver ion as a moiety of the heterocycle. Examples of the former include a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, an imidazole group, a purine group, etc. Examples of the latter include a thiophene group, a thiazole group, an oxazole group, a benzothiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenazole group, a benzoselenazole group, a tellurazole group, a benztellurazole group, etc. The former is preferable.

[0226]

The sulfide group used as the adsorptive group may be any group with a $\cdot\text{S}\cdot$ moiety, and preferably has a moiety of alkyl or alkylene-S-alkyl or alkylene-aryl or arylene-S-alkyl or alkylene; or aryl or arylene-S-aryl or arylene. The sulfide group may form a ring structure, and may be a $\cdot\text{S}\cdot\text{S}\cdot$ group. Specific examples of the ring structure include groups with a thiolane ring, a 1,3-dithiolane ring, a 1,2-dithiolane ring, a thiane ring, a dithiane ring, a tetrahydro-1,4-thiazine ring (a thiomorpholine ring), etc. Particularly preferable as the sulfide groups are groups having a moiety of alkyl or alkylene-S-alkyl or alkylene.

[0227]

The cationic group used as the adsorptive group is a quaternary nitrogen-containing group, specifically a group with an ammonio group or a quaternary nitrogen-containing heterocyclic group. Incidentally, there is no case where the cationic group partly composes an atomic group forming a dye structure, such as a cyanine chromophoric group. The ammonio group may be a trialkylammonio group, a dialkylarylammonio group, an alkyldiarylammonio group, etc., and examples thereof include a benzylidemethylammonio group, a trihexylammonio group, a phenyldiethylammonio group, etc. Examples of the quaternary nitrogen-containing heterocyclic group include a pyridinio group, a quinolinio group, an isoquinolinio group, an imidazolio group, etc. Preferred are a pyridinio group and an imidazolio group, and particularly preferred is a pyridinio group. The quaternary nitrogen-containing heterocyclic group may have an optional substituent. Preferred as the substituent in the case of the pyridinio group and the imidazolio group are alkyl groups, aryl groups, acylamino groups, a chlorine atom, alkoxycarbonyl groups and carbamoyl groups. Particularly preferred as the substituent in the case of the pyridinio group is a phenyl group.

[0228]

The ethynyl group used as the adsorptive group means a $\text{C}\equiv\text{CH}$ group, in which the hydrogen atom may be substituted.

[0229]

The adsorptive group may have an optional substituent.

[0230]

Specific examples of the adsorptive group further include groups described in pages 4 to 7 of a specification of JP-A No. 11-95355.

[0231]

Preferred as the adsorptive group used in the invention are mercapto-substituted, nitrogen-containing, heterocyclic groups such as a 2-mercaptopthiadiazole group, a 3-mercato-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercato-1,3,4-oxadiazole group, a 2-mercaptobenzoxazole group, a 2-mercaptobenzthiazole group and a 1,5-dimethyl-1,2,4-triazolium-3-thiolate group; and nitrogen-containing heterocyclic groups having a -NH- group that can form a silver imide (>NAg) as a moiety of the heterocycle, such as a benzotriazole group, a benzimidazole group and an indazole group. Particularly preferred are a 5-mercaptotetrazole group, a 3-mercato-1,2,4-triazole group and a benzotriazole group, and the most preferred are a 3-mercato-1,2,4-triazole group and a 5-mercaptotetrazole group.

[0232]

Among these compounds, it is particularly preferred that the compound has two or more mercapto groups as a moiety. The mercapto group (-SH) may be converted into a thione group in the case where it can be tautomerized. The compound may have two or more adsorbent groups containing above-mentioned mercapto or thione group as a moiety, such as a cyclic thioamide group, an alkylmercapto group, an arylmercapto group and a heterocyclic mercapto group. Further, the compound may have one or more adsorptive group containing two or

more mercapto or thione groups as a moiety, such as a dimercapto-substituted, nitrogen-containing, heterocyclic group.

[0233]

Examples of the adsorptive group containing two or more mercapto group, such as a dimercapto-substituted, nitrogen-containing, heterocyclic group, include a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group, a 2,5-dimercapto-1,3-oxazole group, a 2,7-dimercapto-5-methyl-*s*-triazolo(1,5-*A*)-pyrimidine group, a 2,6,8-trimercaptopurine group, a 6,8-dimercaptopurine group, a 3,5,7-trimercapto-*s*-triazolotriazine group, a 4,6-dimercaptopyrazolo pyrimidine group, a 2,5-dimercapto-imidazole group, etc. Particularly preferred are a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, and a 3,5-dimercapto-1,2,4-triazole group.

[0234]

The adsorptive group may be connected to any position of the compound represented by each of formulae (A) to (F) and (1) to (3). Preferred portions, which the adsorptive group bonds to, are RED₁₁, RED₁₂, RED₂ and RED₃ in formulae (A) to (D), RED₄₁, R₄₁, RED₄₂, and R₄₆ to R₄₈ in formulae (E) and (F), and optional portions other than R₁, R₂, R₁₁, R₁₂, R₃₁, L₁, L₂₁ and L₃₁ in formulae (1) to (3). Further, more preferred portions are RED₁₁ to RED₄₂ in formulae (A) to (F).

[0235]

The spectral sensitizer moiety is a group containing a spectral sensitizer chromophore, a residual group provided by removing an optional hydrogen atom or substituent from a spectral sensitizer compound. The spectral sensitizer moiety may be connected to any position of the compound represented by each of formulae (A) to (F) and (1) to (3). Preferred portion, which the spectral sensitizer moiety bonds to, are RED_{11} , RED_{12} , RED_2 and RED_3 in formulae (A) to (D), RED_{41} , R_{41} , RED_{42} , and R_{46} to R_{48} in formulae (E) and (F), and optional portions other than R_1 , R_2 , R_{11} , R_{12} , R_{31} , L_1 , L_{21} and L_{31} in formulae (1) to (3). Further, more preferred portions are RED_{11} to RED_{42} in formulae (A) to (F). The spectral sensitizer is preferably such that typically used in color sensitizing techniques. Examples thereof include cyanine dyes, composite cyanine dyes, merocyanine dyes, composite merocyanine dyes, homopolar cyanine dyes, styryl dyes, and hemicyanine dyes. Typical spectral sensitizers are disclosed in Research Disclosure, Item 36544, September 1994. The dyes can be synthesized by one skilled in the art according to procedures described in the above Research Disclosure and F. M. Hamer, *The Cyanine dyes and Related Compounds*, Interscience Publishers, New York, 1964. Further, dyes described in pages 4 to 7 of a specification of JP-A No. 11-95355 (USP No. 6,054,260) may be used in the invention.

[0236]

The compounds of Groups 1 to 4 used in the invention has preferably 10 to 60 carbon atoms in total, more preferably 15 to 50 carbon atoms, furthermore preferably 18 to 40 carbon atoms, particularly preferably 18 to 30 carbon atoms.

[0237]

When a silver halide photosensitive material using the compounds of Groups 1 to 4 is exposed, the compound is one-electron-oxidized. After the subsequent reaction, the compound is further oxidized while releasing one electron, or two or more electrons depending on Group. An oxidation potential in the first one-electron oxidation is preferably 1.4 V or less, more preferably 1.0 V or less. This oxidation potential is preferably 0 V or more, more preferably 0.3 V or more. Thus, the oxidation potential is preferably approximately 0 V to 1.4 V, more preferably approximately 0.3 V to 1.0 V.

[0238]

The oxidation potential may be measured by a cyclic voltammetry technique. Specifically, a sample is dissolved in a solution of acetonitrile/water containing 0.1 M lithium perchlorate = 80/20 (volume %), nitrogen gas is passed through the resultant solution for 10 minutes, and then the oxidation potential is measured at 25 °C at a potential scanning rate of 0.1 V/second by using a glassy carbon disk as a working electrode, using a platinum wire as a counter electrode, and using a calomel electrode (SCE) as a reference electrode. The oxidation potential per SCE is obtained at peak potential of cyclic voltammetric curve.

[0239]

In the case where the compound of Groups 1 to 4 is one-electron-oxidized and release further one electron after the subsequent reaction, an oxidation potential in the subsequent oxidation is preferably -0.5 V to -2 V, more preferably -0.7 V to -2 V, furthermore preferably -0.9 V to -1.6 V.

[0240]

In the case where the compound of Groups 1 to 4 is one-electron-oxidized and release further two or more electrons after the subsequent reaction, oxidation potentials in the subsequent oxidation are not particularly limited. The oxidation potentials in the subsequent oxidation often cannot be measured precisely, because an oxidation potential in releasing the second electron cannot be clearly differentiated from an oxidation potential in releasing the third electron.

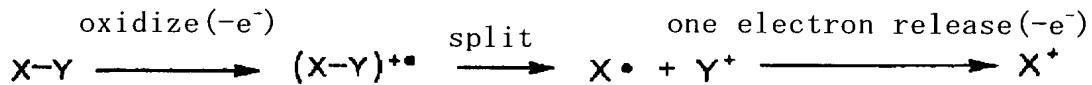
[0241]

Next, the compound of Group 5 will be described.

The compound of Group 5 is represented by X-Y, in which X represents a reducible group and Y represents a leaving group. The reducible group represented by X can be one-electron-oxidized to provide a one-electron oxidation product, which can be converted into an X radical by eliminating the leaving group of Y with a subsequent X-Y bond cleavage reaction. The X radical can release further one electron. The oxidation reaction of the compound of Group T5 may be represented by the following formula.

[0242]

[Formula 23]



[0243]

The compound of Group 5 exhibits an oxidation potential of preferably 0 V to 1.4 V, more preferably 0.3 V to 1.0 V. The radical X· generated in the formula exhibits an oxidation potential of preferably -0.7 V to -2.0 V, more preferably -0.9 V to -1.6 V.

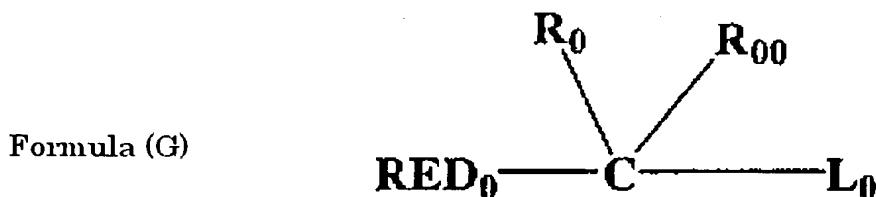
[0244]

The compound of Group 5 is preferably represented by the following formula (G).

[0245]

Formula (G)

[Formula 24]



[0246]

In formula (G), RED₀ represents a reducible group, L₀ represents a leaving group, and R₀ and R₀₀ each represent a hydrogen atom or a substituent. RED₀ and R₀, and R₀ and R₀₀ may be bond together to form a ring structure, respectively. RED₀ is the same as RED₂ in formula (C) with respect to the meanings and preferred embodiments. R₀ and R₀₀ are the same as R₂₁ and R₂₂

in formula (C) with respect to the meanings and preferred embodiments, respectively. Incidentally, R_0 and R_{00} are not the same as the leaving group of L_0 respectively, except for a hydrogen atom. RED_0 and R_0 may bond together to form a ring structure with examples and preferred embodiments the same as those of the ring structure formed by bonding RED_2 and R_{21} in formula (C). Examples of the ring structure formed by bonding R_0 and R_{00} each other include a cyclopentane ring, a tetrahydrofuran ring, etc. In formula (G), L_0 is the same as L_2 in formula (C) with respect to the meanings and preferred embodiments.

[0247]

The compound represented by formula (G) preferably has an adsorptive group to the silver halide or a spectrally sensitizing dye moiety. However, the compound does not have two or more adsorptive groups when L_0 is a group other than a silyl group. Incidentally, the compound may have two or more sulfide groups as the adsorbent groups, not depending on L_0 .

[0248]

The adsorptive group to the silver halide in the compound represented by formula (G) may be the same as those in the compounds of Groups 1 to 4, and further may be the same as all of the compounds and preferred embodiments described as "an adsorptive group to the silver halide" in pages 4 to 7 of a specification of JP-A No. 11-95355.

[0249]

The spectral sensitizer moiety in the compound represented by formula

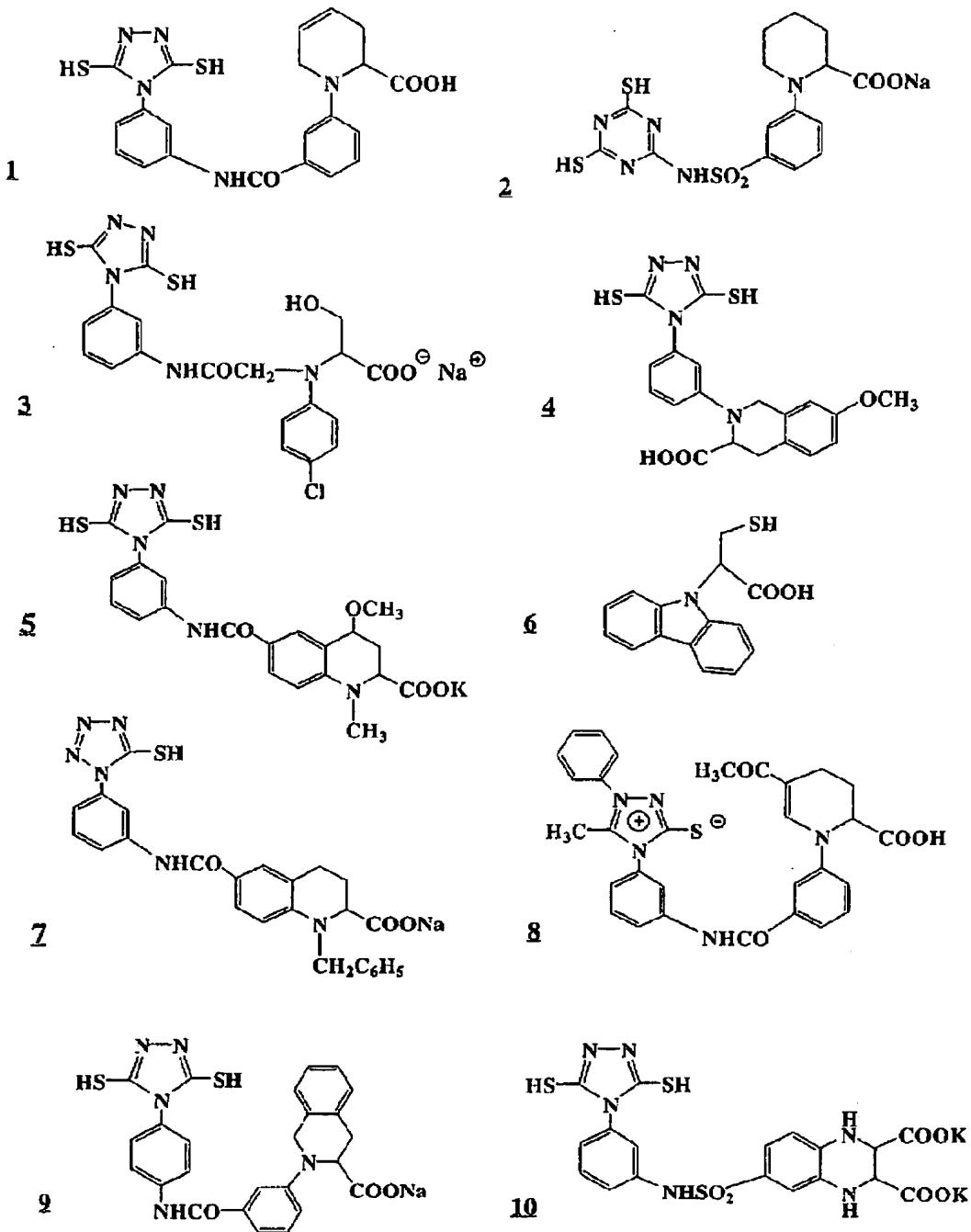
(G) is the same as in the compounds of Groups 1 to 4, and may be the same as all of the compounds and preferred embodiments described as "photoabsorptive group" in pages 7 to 14 of a specification of JP-A No. 11-95355.

[0250]

Specific examples of the compounds of Groups 1 to 5 used in the invention are illustrated below without intention of restricting the scope of the invention.

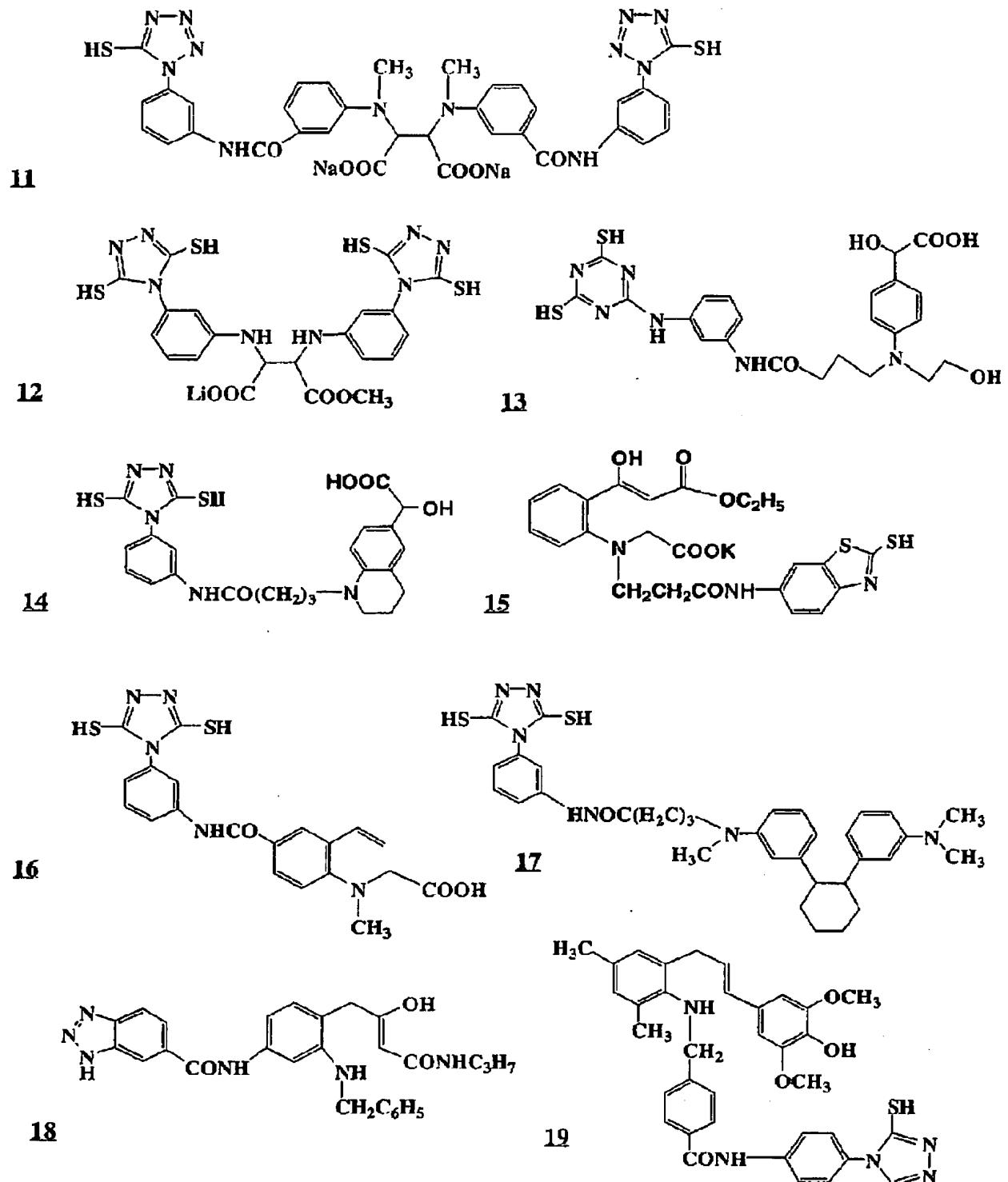
[0251]

[Formula 25]



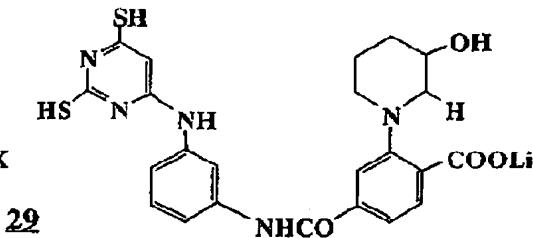
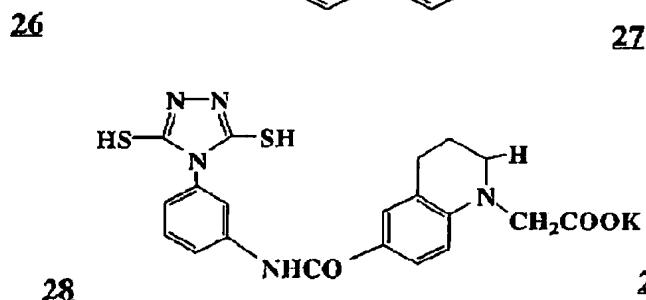
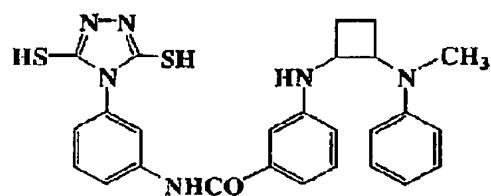
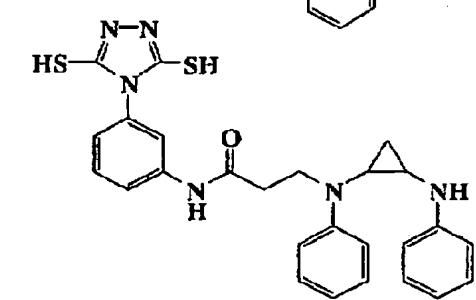
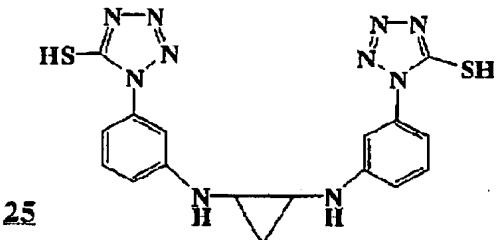
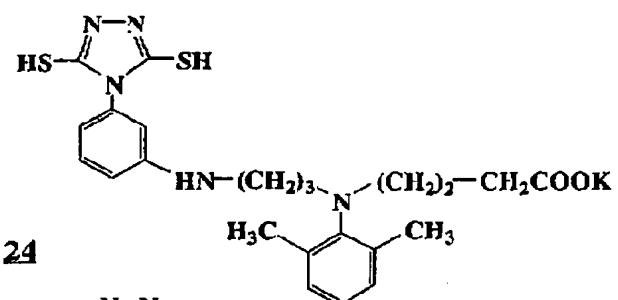
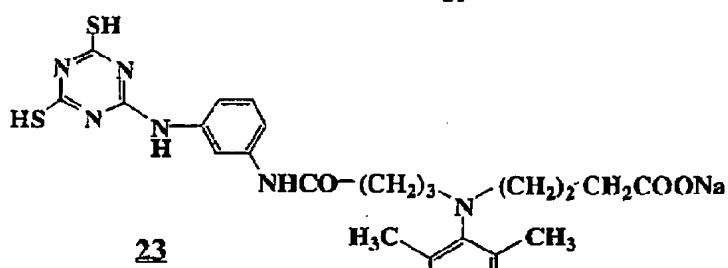
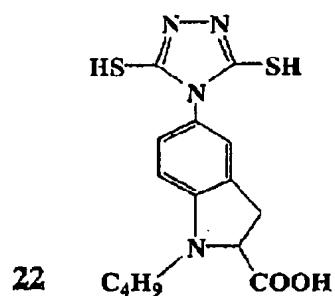
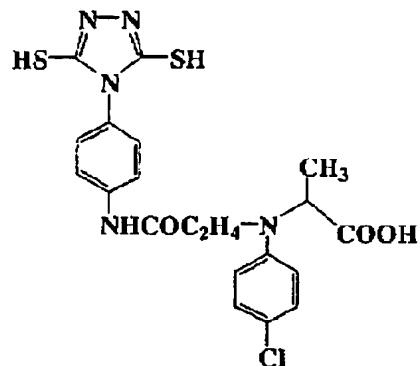
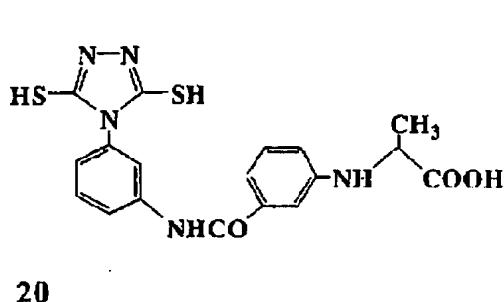
[0252]

[Formula 26]



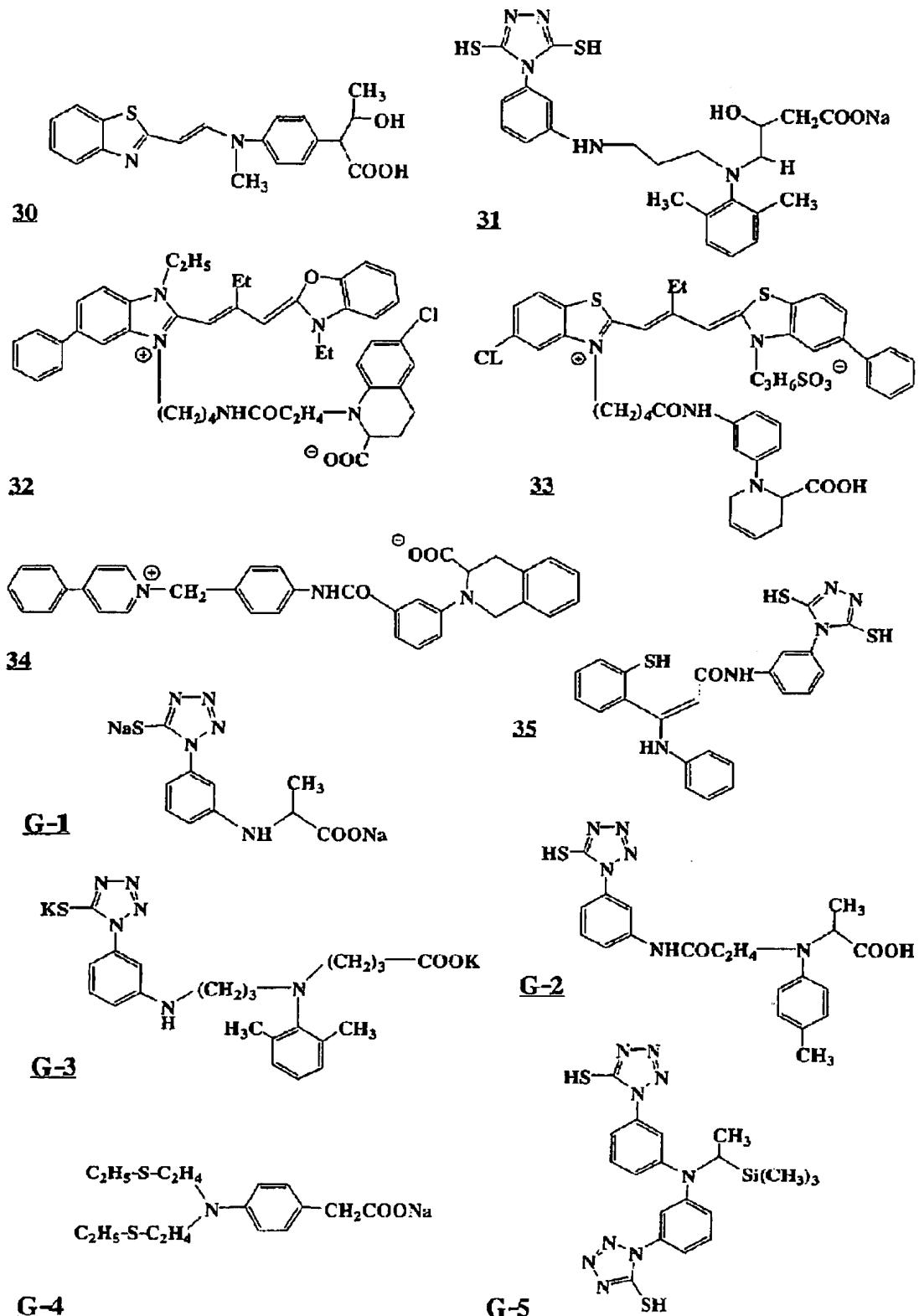
[0253]

[Formula 27]



[0254]

[Formula 28]



[0255]

The compounds of Groups 1 to 4 used in the invention are the same as compounds described in detail in Japanese Patent Application Nos. 2002-192373, 2002-188537, 2002-188536, 2001-272137, and 2002-192374, respectively. The specific examples of the compounds of Groups 1 to 4 used in the invention further include compound examples disclosed in the specifications. Synthesis examples of the compounds of Groups 1 to 4 used in the invention may be the same as described in the specifications.

[0256]

Specific examples of the compounds of Group 5 further include examples of compound referred to as "one photon two electrons sensitizer" or "deprotonating electron-donating sensitizer" described in JP-A No. 9-211769 (Compound PMT 1 to S-37 in Tables E and F, pages 28 to 32); JP-A No. 9-211774; JP-A No. 11-95355 (Compound INV 1 to 36); JP-W No. 2001-500996 (Compound 1 to 74, 80 to 87, and 92 to 122); USP Nos. 5747235 and 5747236; EP No. 786692 A1 (Compound INV 1 to 35); EP No. 893732 A1; USP Nos. 6054260 and 5994051; etc.

[0257]

The compounds of Groups 1 to 5 may be used at any time during preparation of the photosensitive silver halide emulsion and production of the photothermographic material. For example, the compound may be used, in a photosensitive silver halide grain formation step, in a desalting step, in a chemical sensitization step, and before coating, etc. The compound may be

added in several times, during these steps. The compound is preferably added, after the photosensitive silver halide grain formation step and before the desalting step; in the chemical sensitization step (just before the chemical sensitization to immediately after the chemical sensitization); or before coating. The compound is more preferably added, just before the chemical sensitization step to before mixing with the non-photosensitive organic silver salt.

[0258]

It is preferred that the compound of Groups 1 to 5 used in the invention is dissolved in water, a water-soluble solvent such as methanol and ethanol, or a mixed solvent thereof, to be added. In the case where the compound is dissolved in water and solubility of the compound is increased by increasing or decreasing a pH value of the solvent, the pH value may be increased or decreased to dissolve and add the compound.

[0259]

The compound of Groups 1 to 5 used in the invention is preferably added to the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt. The compound may be added to a surface protective layer, or an intermediate layer, as well as the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt, to be diffused to the image forming layer in the coating step. The compound may be added before or after addition of a sensitizing dye. A mol value of the compound per one mol of the silver halide is preferably 1×10^{-9} mol to 5×10^{-1} mol, more preferably 1×10^{-8} mol to 5×10^{-2} mol, in a layer comprising

the photosensitive silver halide emulsion.

[0260]

10) Combined use of a plurality of silver halides

The photosensitive silver halide emulsion in the photosensitive material used in the invention may be used alone, or two or more kinds of them (for example, those of different average particle sizes, different halogen compositions, of different crystal habits and of different conditions for chemical sensitization) may be used together. Gradation can be controlled by using plural kinds of photosensitive silver halide of different sensitivity. The relevant techniques can include those described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627, and 57-150841. It is preferred to provide a sensitivity difference of 0.2 or more in terms of $\log E$ between each of the emulsions.

[0261]

11) Coating amount

The addition amount of the photosensitive silver halide, when expressed by the coating amount of silver per one m^2 of the photothermographic material, is preferably from 0.03 g/m^2 to 0.6 g/m^2 , more preferably, 0.05 g/m^2 to 0.4 g/m^2 and, further preferably, 0.07 g/m^2 to 0.3 g/m^2 . The photosensitive silver halide is used by 0.01 mol to 0.5 mol, preferably, 0.02 mol to 0.3 mol, and further preferably 0.03 mol to 0.2 mol per one mol of the organic silver salt.

[0262]

12) Mixing silver halide and organic silver salt

The method of mixing the silver halide and the organic silver salt can include a method of mixing a separately prepared photosensitive silver halide and an organic silver salt by a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or homogenizer, or a method of mixing a photosensitive silver halide completed for preparation at any timing in the preparation of an organic silver salt and preparing the organic silver salt. The effect of the invention can be obtained preferably by any of the methods described above. Further, a method of mixing two or more kinds of aqueous dispersions of organic silver salts and two or more kinds of aqueous dispersions of photosensitive silver salts upon mixing is used preferably for controlling the photographic properties.

[0263]

13) Mixing silver halide into coating solution

In the invention, the time of adding silver halide to the coating solution for the image forming layer is preferably in the range from 180 minutes before to just prior to the coating, more preferably, 60 minutes before to 10 seconds before coating. But there is no restriction for mixing method and mixing condition as far as the effect of the invention appears sufficient. As an embodiment of a mixing method, there is a method of mixing in the tank controlling the average residence time to be desired. The average residence time herein is calculated from addition flux and the amount of solution transferred to the coater. And another embodiment of mixing method is a method using a static mixer, which is described in 8th edition of "Ekitai kongou gijutsu" by N. Harnby and M.F. Edwards, translated by Kouji Takahashi (Nikkankougyou shinbunsha, 1989).

[0264]

1-7. Binder

Any type of polymer may be used as the binder for the layer containing organic silver salt in the photothermographic material of the invention.

Suitable as the binder are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymer; or media forming a film; for example, included are gelatin, rubber, poly (vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly (vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal)(e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(ester), poly(urethane), phenoxy resin, poly(vinylidene chloride), poly(epoxide), poly(carbonate), poly(vinyl acetate), poly(olefin), cellulose esters, and poly(amide). A binder may be used with water, an organic solvent or emulsion to form a coating solution.

[0265]

In the invention, the Tg of the binder of the layer including organic silver salts is preferably from 0°C to 80°C, more preferably, from 10°C to 70°C, further preferably, from 15°C to 60°C.

[0266]

In the specification, Tg was calculated according to the following equation.

$$1/T_g = \sum (X_i/T_{gi})$$

Where, the polymer is obtained by copolymerization of n monomer compounds (from $i=1$ to $i=n$); X_i represents the mass fraction of the i th monomer ($\sum X_i=1$), and T_{gi} is the glass transition temperature (absolute temperature) of the homopolymer obtained with the i th monomer. The symbol Σ stands for the summation from $i=1$ to $i=n$. Values for the glass transition temperature (T_{gi}) of the homopolymers derived from each of the monomers were obtained from J. Brandrup and E.H. Immergut, *Polymer Handbook* (3rd Edition)(Wiley-Interscience, 1989).

[0267]

The polymer used for the binder maybe of two or more kinds of polymers, if necessary. And, the polymer having T_g more than $20^\circ C$ and the polymer having T_g less than $20^\circ C$ can be used in combination. In a case that two types or more of polymers differing in T_g may be blended for use, it is preferred that the weight-average T_g is in the range mentioned above.

[0268]

In the invention, it is preferred that the layer containing organic silver salt is formed by first applying a coating solution containing 30% by mass or more of water in the solvent and by then drying.

[0269]

In the case the layer containing organic silver salt is formed by first applying a coating solution containing 30% by mass or more of water in the

solvent and by then drying, and furthermore, in the case the binder of the layer containing organic silver salt is soluble or dispersible in an aqueous solvent (water solvent), the performance can be ameliorated particularly in the case a polymer latex having an equilibrium water content of 2% by mass or lower under 25°C and 60%RH is used. Most preferred embodiment is such prepared to yield an ion conductivity of 2.5 mS/cm or lower, and as such a preparation method, there can be mentioned a refining treatment using a separation function membrane after synthesizing the polymer.

[0270]

The aqueous solvent in which the polymer is soluble or dispersible, as referred herein, signifies water or water containing mixed therein 70% by mass or less of a water-admixing organic solvent. As water-admixing organic solvents, there can be mentioned, for example, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and the like; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and the like; ethyl acetate, dimethylformamide, and the like.

[0271]

The term aqueous solvent is also used in the case the polymer is not thermodynamically dissolved, but is present in a so-called dispersed state.

[0272]

The term "equilibrium water content under 25°C and 60%RH" as referred herein can be expressed as follows:

Equilibrium water content under 25°C and 60%RH
=[(W1 – W0)/W0] × 100 (% by mass)
wherein, W1 is the mass of the polymer in moisture-controlled equilibrium under the atmosphere of 25°C and 60%RH, and W0 is the absolutely dried mass at 25°C of the polymer.

[0273]

For the definition and the method of measurement for water content, reference can be made to Polymer Engineering Series 14, "Testing methods for polymeric materials" (The Society of Polymer Science, Japan, published by Chijin Shokan).

[0274]

The equilibrium water content under 25°C and 60%RH is preferably 2% by mass or lower, but is more preferably, 0.01% by mass to 1.5% by mass, and is most preferably, 0.02% by mass to 1% by mass.

[0275]

The binders used in the invention are, particularly preferably, polymers capable of being dispersed in aqueous solvent. Examples of dispersed states may include a latex, in which water-insoluble fine particles of hydrophobic polymer are dispersed, or such in which polymer molecules are dispersed in molecular states or by forming micelles, but preferred are latex-dispersed particles. The average particle size of the dispersed particles is in the range from 1 nm to 50,000 nm, preferably 5 nm to 1,000 nm, more preferably 10 nm to

500 nm, and further preferably 50 nm to 200 nm. There is no particular limitation concerning particle size distribution of the dispersed particles, and may be widely distributed or may exhibit a monodisperse particle size distribution. From the viewpoint of controlling the physical properties of the coating solution, preferred mode of usage includes mixing two or more types of particles each having monodisperse particle distribution.

[0276]

In the invention, preferred embodiment of the polymers capable of being dispersed in aqueous solvent includes hydrophobic polymers such as acrylic polymers, poly(ester), rubber (e.g., SBR resin), poly(urethane), poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride), poly(olefin), and the like. As the polymers above, usable are straight chain polymers, branched polymers, or crosslinked polymers; also usable are the so-called homopolymers in which single monomer is polymerized, or copolymers in which two or more types of monomers are polymerized. In the case of a copolymer, it may be a random copolymer or a block copolymer. The molecular weight of these polymers is, in number average molecular weight, in the range from 5,000 to 1,000,000, preferably from 10,000 to 200,000. Those having too small molecular weight exhibit insufficient mechanical strength on forming the image forming layer, and those having too large molecular weight are also not preferred because the filming properties result poor. Further, crosslinking polymer latexes are particularly preferred for use.

[0277]

(Examples of latex)

Specific examples of preferred polymer latexes are given below, which are expressed by the starting monomers with % by mass given in parenthesis. The molecular weight is given in number average molecular weight. In the case polyfunctional monomer is used, the concept of molecular weight is not applicable because they build a crosslinked structure. Hence, they are denoted as "crosslinking", and the molecular weight is omitted. Tg represents glass transition temperature.

[0278]

P-1; Latex of -MMA(70)-EA(27)-MAA(3)- (molecular weight 37000, Tg 61°C)

P-2; Latex of -MMA(70)-2EHA(20)-St(5)-AA(5)- (molecular weight 40000, Tg 59 °C)

P-3; Latex of -St(50)-Bu(47)-MAA(3)- (crosslinking, Tg -17°C)

P-4; Latex of -St(68)-Bu(29)-AA(3)- (crosslinking, Tg 17°C)

P-5; Latex of -St(71)-Bu(26)-AA(3)- (crosslinking, Tg 24°C)

P-6; Latex of -St(70)-Bu(27)-IA(3)- (crosslinking)

P-7; Latex of -St(75)-Bu(24)-AA(1)- (crosslinking, Tg 29°C)

P-8; Latex of -St(60)-Bu(35)-DVB(3)-MAA(2)-
(crosslinking)

P-9; Latex of -St(70)-Bu(25)-DVB(2)-AA(3)-
(crosslinking)

P-10; Latex of -VC(50)-MMA(20)-EA(20)-AN(5)-AA(5)- (molecular weight 80000)

P-11; Latex of -VDC(85)-MMA(5)-EA(5)-MAA(5)- (molecular weight 67000)

P-12; Latex of -Et(90)-MAA(10)- (molecular weight 12000)

P-13; Latex of -St(70)-2EHA(27)-AA(3)- (molecular weight 130000, Tg 43°C)

P-14; Latex of -MMA(63)-EA(35)-AA(2)- (molecular weight 33000, Tg 47°C)

P-15; Latex of -St(70.5)-Bu(26.5)-AA(3)-
(crosslinking, Tg 23°C)

P-16; Latex of -St(69.5)-Bu(27.5)-AA(3)-
(crosslinking, Tg 20.5°C)

[0279]

In the structures above, abbreviations represent monomers as follows.

MMA: methyl metacrylate, EA: ethyl acrylate, MAA: methacrylic acid, 2EHA: 2-ethylhexyl acrylate, St: styrene, Bu: butadiene, AA: acrylic acid, DVB: divinylbenzene, VC: vinyl chloride, AN: acrylonitrile, VDC: vinylidene chloride, Et: ethylene, IA: itaconic acid.

[0280]

The polymer latexes above are commercially available, and polymers below are usable. As examples of acrylic polymers, there can be mentioned Cevian A-4635, 4718, and 4601 (all manufactured by Daicel Chemical Industries, Ltd.), Nipol Lx811, 814, 821, 820, and 857 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(ester), there can be mentioned FINETEX

ES650, 611, 675, and 850 (all manufactured by Dainippon Ink and Chemicals, Inc.), WD-size and WMS (all manufactured by Eastman Chemical Co.), and the like; as examples of poly(urethane), there can be mentioned HYDRAN AP10, 20, 30, and 40 (all manufactured by Dainippon Ink and Chemicals, Inc.), and the like; as examples of rubber, there can be mentioned LACSTAR 7310K, 3307B, 4700H, and 7132C (all manufactured by Dainippon Ink and Chemicals, Inc.), Nipol Lx416, 410, 438C, and 2507 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinyl chloride), there can be mentioned G351 and G576 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinylidene chloride), there can be mentioned L502 and L513 (all manufactured by Asahi Chemical Industry Co., Ltd.), and the like; as examples of poly(olefin), there can be mentioned Chemipearl S120 and SA100 (all manufactured by Mitsui Petrochemical Industries, Ltd.), and the like.

[0281]

The polymer latexes above may be used alone, or may be used by blending two types or more depending on needs.

[0282]

(Preferable latex)

Particularly preferable as the polymer latex for use in the invention is that of styrene-butadiene copolymer. The mass ratio of monomer unit for styrene to that of butadiene constituting the styrene-butadiene copolymer is preferably in the range of from 40:60 to 95:5. Further, the monomer unit of styrene and that of butadiene preferably account for 60 % by mass to 99 % by

mass with respect to the copolymer. Moreover, the polymer latex of the invention contains acrylic acid or methacrylic acid, preferably, in the range from 1% by mass to 6% by mass, and more preferably, from 2% by mass to 5% by mass, with respect to the total weight of the monomer unit of styrene and that of butadiene. The preferred range of the molecular weight is the same as that described above.

[0283]

As the latex of styrene-butadiene copolymer preferably used in the invention, there can be mentioned P-3 to P-8 and P-15, or commercially available LACSTAR-3307B, 7132C, Nipol Lx416, and the like.

[0284]

In the layer containing organic silver salt of the photosensitive material according to the invention, if necessary, there can be added hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and the like. The hydrophilic polymers above are added at an amount of 30% by mass or less, preferably 20% by mass or less, with respect to the total mass of the binder incorporated in the layer containing organic silver salt.

[0285]

According to the invention, the layer containing organic silver salt (image forming layer) is preferably formed by using polymer latex for the binder. According to the amount of the binder for the layer containing organic silver salt,

the mass ratio for total binder to organic silver salt (total binder/organic silver salt) is preferably in the range of 1/10 to 10/1, more preferably 1/3 to 5/1, and further preferably 1/1 to 3/1.

[0286]

The layer containing organic silver salt is, in general, a photosensitive layer (image forming layer) containing a photosensitive silver halide, i.e., the photosensitive silver salt; in such a case, the mass ratio for total binder to silver halide (total binder/silver halide) is in the range of from 400 to 5, more preferably, from 200 to 10.

[0287]

The total amount of binder in the image forming layer of the invention is preferably in the range from 0.2 g/m² to 30 g/m², more preferably from 1 g/m² to 15 g/m², and further preferably from 2 g/m² to 10 g/m². As for the image forming layer of the invention, there may be added a crosslinking agent for crosslinking, or a surfactant and the like to improve coating properties.

[0288]

(Preferable solvent for coating solution)

In the invention, a solvent of a coating solution for a layer containing organic silver salt (wherein a solvent and water are collectively described as a solvent for simplicity) is preferably an aqueous solvent containing water at 30% by mass or more. Examples of solvents other than water may include any of water-miscible organic solvents such as methyl alcohol, ethyl alcohol, isopropyl

alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide and ethyl acetate. A water content in a solvent is more preferably 50% by mass or more and still more preferably 70% by mass or more. Concrete examples of a preferable solvent composition, in addition to water=100, are compositions in which methyl alcohol is contained at ratios of water/methyl alcohol = 90/10 and 70/30, in which dimethylformamide is further contained at a ratio of water/methyl alcohol/dimethylformamide = 80/15/5, in which ethyl cellosolve is further contained at a ratio of water/methyl alcohol/ethyl cellosolve = 85/10/5, and in which isopropyl alcohol is further contained at a ratio of water/methyl alcohol/isopropyl alcohol = 85/10/5 (wherein the numerals presented above are values in % by mass).

[0289]

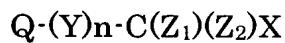
1-8. Antifoggant

1) Organic polyhalogen compound

In the invention, the organic polyhalogen compound represented by formula (H) described below is preferably used as the antifoggant in combination with the compound represented by formulae (1a), (1b) or (1c).

[0290]

Formula (H)



In formula (H), Q represents an alkyl group, an aryl group, or a heterocyclic group; Y represents a divalent connecting group; n represents 0 or 1; Z₁ and Z₂ each represent a halogen atom; and X represents hydrogen atom or an

electron-attracting group.

[0291]

In formula (H), Q preferably is a phenyl group substituted by an electron-attracting group whose Hammett substitution coefficient σ_p yields a positive value. For the details of Hammett substitution coefficient, reference can be made to *Journal of Medicinal Chemistry*, Vol. 16, No. 11 (1973), pp. 1207 to 1216, and the like.

[0292]

As such electron-attracting groups, examples include, halogen atoms (fluorine atom (σ_p value: 0.06), chlorine atom (σ_p value: 0.23), bromine atom (σ_p value: 0.23), iodine atom (σ_p value: 0.18)), trihalomethyl groups (tribromomethyl (σ_p value: 0.29), trichloromethyl (σ_p value: 0.33), trifluoromethyl (σ_p value: 0.54)), a cyano group (σ_p value: 0.66), a nitro group (σ_p value: 0.78), an aliphatic aryl or heterocyclic sulfonyl group (for example, methanesulfonyl (σ_p value: 0.72)), an aliphatic aryl or heterocyclic acyl group (for example, acetyl (σ_p value: 0.50) and benzoyl (σ_p value: 0.43)), an alkinyl (e.g., $\text{C}\equiv\text{CH}$ (σ_p value: 0.23)), an aliphatic aryl or heterocyclic oxycarbonyl group (e.g., methoxycarbonyl (σ_p value: 0.45) and phenoxy carbonyl (σ_p value: 0.44)), a carbamoyl group (σ_p value: 0.36), sulfamoyl group (σ_p value: 0.57), sulfoxido group, heterocyclic group, and phosphoryl group.

Preferred range of the σ_p value is from 0.2 to 2.0, and more preferably, from 0.4 to 1.0.

[0293]

Preferred as the electron-attracting groups are a carbamoyl group, an alkoxy carbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, a carboxyl group, an alkylcarbonyl group, and an arylcarbonyl group, particularly preferred among them are a carbamoyl group, an alkoxy carbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, and most preferred among them is a carbamoyl group.

[0294]

X preferably is an electron-attracting group, more preferably, a halogen atom, an aliphatic aryl or heterocyclic sulfonyl group, an aliphatic aryl or heterocyclic acyl group, an aliphatic aryl or heterocyclic oxycarbonyl group, carbamoyl group, or sulfamoyl group; particularly preferred among them is a halogen atom.

Among halogen atoms, preferred are chlorine atom, bromine atom, and iodine atom; more preferred are chlorine atom and bromine atom; and particularly preferred is bromine atom.

[0295]

Y preferably represents $-C(=O)\cdot$, $\cdot SO\cdot$, or $\cdot SO_2\cdot$; more preferably, $-C(=O)\cdot$ or $\cdot SO_2\cdot$; and particularly preferred is $\cdot SO_2\cdot$. n represents 0 or 1, and preferred is 1.

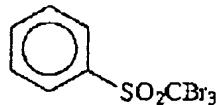
[0296]

Specific examples of the compounds expressed by formula (H) of the invention are shown below.

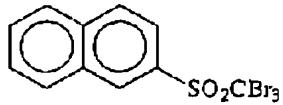
[0297]

[Formula 29]

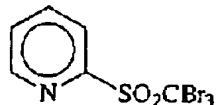
(H-1)



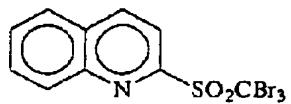
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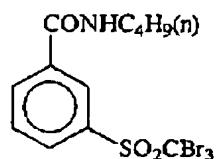
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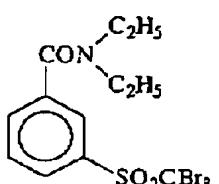
(H-4)



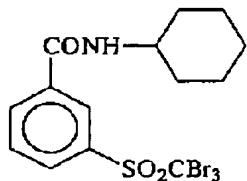
(H-5)



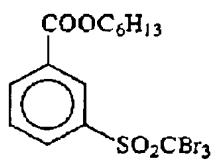
(H-6)



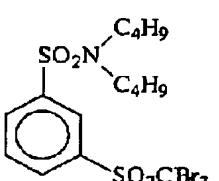
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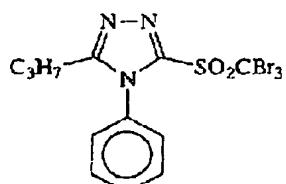
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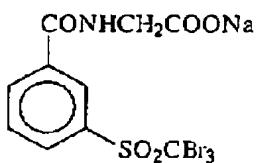
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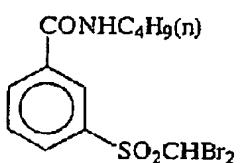
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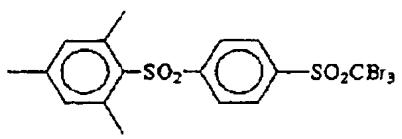
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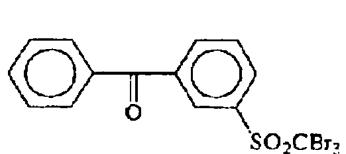
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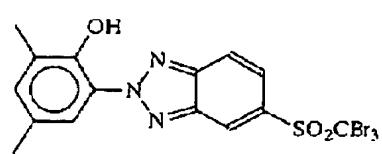
(H-13)



(H-14)



(H-15)



[0298]

A compound expressed by formula (H) in the invention is preferably used in the range from 10^{-4} mol to 0.8 mol per one mole of a non-photosensitive silver salt in an image forming layer, more preferably used in the range from 10^{-3} mol to 0.1 mol and still more preferably used in the range from 5×10^{-3} mol to 0.05 mol.

[0299]

The addition ratio for the compound represented by formula (H) of the invention to the compounds represented by formulae (1a), (1b) and (1c) of the invention $[(H) / (1a+1b+1c)]$ is preferably in the range from 90/10 to 0/100, and more preferably from 50/50 to 0/100.

[0300]

In the invention, a method of incorporating a compound expressed by formula (H) into a photosensitive material is described in a method of incorporating a reducing agent described above.

[0301]

A melting point of a compound expressed by formula (H) is preferably 200°C or lower and more preferably 170°C or lower.

[0302]

Examples of other organic polyhalogen compounds used in the invention are disclosed in paragraphs Nos. 0111 to 0112 of JP-A No. 11-65021. Preferable examples thereof are an organic polyhalogen compound expressed by formula (P)

described in Japanese Patent Application No. 11-87297, an organic polyhalogen compound expressed by formula (II) described in JP-A No. 10-339934 and an organic polyhalogen compound described in Japanese Patent Application No. 11-205330.

[0303]

2) Other antifoggants

As other antifoggants, there can be mentioned a mercury (II) salt described in paragraph number 0113 of JP-A No. 11-65021, benzoic acids described in paragraph number 0114 of the same literature, a salicylic acid derivative described in JP-A No. 2000-206642, a formaline scavenger compound expressed by formula (S) in JP-A No. 2000-221634, a triazine compound related to Claim 9 of JP-A No. 11-352624, a compound expressed by formula (III), 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and the like, as described in JP-A No. 6-11791.

[0304]

As an antifoggant, stabilizer and stabilizer precursor usable in the invention, there can be mentioned those disclosed as patents in paragraph number 0070 of JP-A No. 10-62899 and in line 57 of page 20 to line 7 of page 21 of EP-A No. 0803764A1, the compounds described in JP-A Nos. 9-281637 and 9-329864.

[0305]

The photothermographic material of the invention may further contain

an azonium salt in order to prevent fogging. As azonium salts, there can be mentioned a compound expressed by formula (XI) as described in JP-A No. 59-193447, a compound described in JP-B No. 55-12581, and a compound expressed by formula (II) in JP-A No. 60-153039. The azonium salt may be added to any part of the photosensitive material, but as the addition layer, preferred is to select a layer on the side having thereon the photosensitive layer, and more preferred is to select a layer containing organic silver salt.

[0306]

The azonium salt may be added at any time of the process of preparing the coating solution; in the case the azonium salt is added into the layer containing the organic silver salt, any time of the process may be selected, from the preparation of the organic silver salt to the preparation of the coating solution, but preferred is to add the salt after preparing the organic silver salt and just before the coating. As the method for adding the azonium salt, any method using a powder, a solution, a fine-particle dispersion, and the like, may be used. Furthermore, it may be added as a solution having mixed therein other additives such as sensitizing agents, reducing agents, toner, and the like.

[0307]

In the invention, the azonium salt may be added at any amount, but preferably, it is added in the range from 1×10^{-6} mol to 2 mol, and more preferably, from 1×10^{-3} mol to 0.5 mol per one mol of silver.

[0308]

1·8. Other additives

1) Mercapto compounds, disulfides and thiones

In the invention, mercapto compounds, disulfide compounds, and thione compounds may be added in order to control the development by suppressing or enhancing development, to improve spectral sensitization efficiency, and to improve storage properties before and after development. Descriptions can be found in paragraph Nos. 0067 to 0069 of JP·A No. 10·62899, a compound expressed by formula (I) of JP·A No. 10·186572 and specific examples thereof shown in paragraph Nos. 0033 to 0052, in lines 36 to 56 in page 20 of EP No. 0803764A1. Among them, mercapto-substituted heterocyclic aromatic compound, which is described in JP·A Nos. 9·297367, 9·304875, 2001·100358, Japanese Patent Application Nos. 2001·104213 and 2001·104214 and the like, is particularly preferred.

[0309]

2) Toner

In the photothermographic material of the present invention, the addition of a toner is preferred. The description of the toner can be found in JP·A No.10·62899 (paragraph Nos. 0054 to 0055), EP·A No.0803764A1 (page21, lines 23 to 48), JP·A Nos.2000·356317 and 2000·187298. Preferred are phthalazinones (phthalazinone, phthalazinone derivatives and metal salts thereof, e.g.,4·(1-naphthyl)phthalazinone,6·chlorophthalazinone, 5,7·dimethoxyphthalazinone and 2,3·dihydro·1,4·phthalazinedione); combinations of phthalazinones and phthalic acids(e.g., phthalic acid, 4·methylphthalic acid, 4·nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and

tetrachlorophthalic anhydride); phthalazines(phthalazine, phthalazine derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-tert-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine); combinations of phthalazines and phthalic acids. Particularly preferred is a combination of phthalazines and phthalic acids. Among them, particularly preferable are the combination of 6-isopropylphthalazine and phthalic acid, and the combination of 6-isopropylphthalazine and 4-methylphthalic acid.

[0310]

3) Plasticizer and lubricant

Plasticizers and lubricants usable in the photothermographic material of the invention are described in paragraph No. 0117 of JP-A No. 11-65021.

Lubricants are described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and paragraph Nos. 0049 to 0062 of Japanese Patent Application No. 11-106881.

[0311]

4) Dyes and pigments

From the viewpoint of improving image tone, preventing the generation of interference fringes and preventing irradiation on laser exposure, various types of dyes and pigments (for instance, C.I. Pigment Blue 60, C.I. Pigment Blue 64, and C.I. Pigment Blue 15:6) may be used in the photosensitive layer of the invention. Detailed description can be found in WO No. 98/36322, JP-A Nos. 10-268465 and 11-338098, and the like.

[0312]

5) Ultra-high contrast promoting agent

In order to form ultra-high contrast image suitable for use in graphic arts, it is preferred to add an ultra-high contrast promoting agent into the image forming layer. Details on the ultra-high contrast promoting agents, method of their addition and addition amount can be found in paragraph No. 0118, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in Japanese Patent Application No. 11-87297, compounds expressed by formulae (III) to (V) (Formulae 21 to 24) of Japanese Patent Application No. 11-91652; as an ultra-high contrast accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0313]

In the case of using formic acid or formates as a strong fogging agent, it is preferably incorporated into the side having thereon the image forming layer containing photosensitive silver halide, at an amount of 5 mmol or less, preferably, 1 mmol or less per one mol of silver.

[0314]

In the case of using an ultra-high contrast promoting agent in the photothermographic material of the invention, it is preferred to use an acid resulting from hydration of diphosphorus pentaoxide, or its salt in combination. Acids resulting from the hydration of diphosphorus pentaoxide or salts thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric

acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt), and the like. Particularly preferred acids obtainable by the hydration of diphosphorus pentaoxide or salts thereof include orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specifically mentioned as the salts are sodium orthophosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate, and the like.

[0315]

The amount of usage of the acid obtained by hydration of diphosphorus pentaoxide or the salt thereof (i.e., the coverage per 1 m² of the photosensitive material) may be set as desired depending on the sensitivity and fogging, but preferred is an amount of 0.1 mg/m² to 500 mg/m², and more preferably, of 0.5 mg/m² to 100 mg/m².

[0316]

The reducing agent, hydrogen bonding compound, development accelerator, and the organic polyhalogen compounds according to the invention are preferably used as solid dispersions, and the method of preparing the solid dispersion is described in JP-A No. 2002-55405.

[0317]

1.9. Preparation of coating solution

The temperature for preparing the coating solution for use in the image forming layer of the invention is preferably from 30°C to 65°C, more preferably,

from 35°C or more to less than 60°C, and further preferably, from 35°C to 55°C. Furthermore, the temperature of the coating solution for the image forming layer immediately after adding the polymer latex is preferably maintained in the temperature range from 30°C to 65°C.

[0318]

1-10. Layer constitution and Components

The image forming layer of the invention is constructed on a support by one or more layers. In the case of constituting the layer by a single layer, it comprises an organic silver salt, photosensitive silver halide, a reducing agent, and a binder, which may further comprise additional materials as desired if necessary, such as a toner, a coating aid, and other auxiliary agents. In the case of constituting the image forming layer from two or more layers, the first image forming layer (in general, a layer placed adjacent to the support) contains an organic silver salt and a photosensitive silver halide, and some of the other components must be incorporated in the second image forming layer or in both of the layers. The constitution of a multicolor photothermographic material may include combinations of two layers for those for each of the colors, or may contain all the components in a single layer as described in USP No. 4708928. In the case of multicolor photothermographic material, each of the image forming layers is maintained distinguished from each other by incorporating functional or non-functional barrier layer between each of the photosensitive layers as described in USP No. 4460681.

[0319]

The photothermographic material according to the invention may have a non-photosensitive layer in addition to the image forming layer. The non-photosensitive layers can be classified depending on the layer arrangement into (a) a surface protective layer provided on the image forming layer (on the side farther from the support), (b) an intermediate layer provided among plural image forming layers or between the image forming layer and the protective layer, (c) an undercoat layer provided between the image forming layer and the support, and (d) a back layer provided to the side opposite to the image forming layer.

[0320]

Furthermore, a layer that functions as an optical filter may be provided as (a) or (b) above. An antihalation layer may be provided as (c) or (d) to the photosensitive material.

[0321]

1) Surface protective layer

The photothermographic material of the invention may further comprise a surface protective layer with an object to prevent adhesion of the image forming layer. The surface protective layer may be a single layer, or plural layers.

[0322]

Description on the surface protective layer may be found in paragraph Nos. 0119 to 0120 of JP-A No. 11-65021 and in JP-A No. 2000-171936.

[0323]

Preferred as the binder of the surface protective layer of the invention is gelatin, but polyvinyl alcohol (PVA) may be used preferably instead, or in combination. As gelatin, there can be used an inert gelatin (e.g., Nitta gelatin 750), a phthalated gelatin (e.g., Nitta gelatin 801), and the like. Usable as PVA are those described in paragraph Nos. 0009 to 0020 of JP-A No. 2000-171936, and preferred are the completely saponified product PVA-105 and the partially saponified PVA-205 and PVA-335, as well as modified polyvinyl alcohol MP-203 (trade name of products from Kuraray Ltd.). The coating amount of polyvinyl alcohol (per 1 m² of support) in the protective layer (per one layer) is preferably in the range from 0.3 g/m² to 4.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

[0324]

The coating amount (per 1 m² of support) of the total binder (including aqueous polymer and latex polymer) in the surface protective layer (per one layer) is preferably in the range from 0.3 g/m² to 5.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

[0325]

2) Antihalation layer

The photothermographic material of the present invention may comprise an antihalation layer provided to the side farther from the light source with respect to the photosensitive layer.

[0326]

Descriptions on the antihalation layer can be found in paragraph Nos. 0123 to 0124 of JP-A No. 11-65021, in JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, 11-352626, and the like.

[0327]

The antihalation layer contains an antihalation dye having its absorption at the wavelength of the exposure light. In the case the exposure wavelength is in the infrared region, an infrared-absorbing dye may be used, and in such a case, preferred are dyes having no absorption in the visible region.

[0328]

In the case of preventing halation from occurring by using a dye having absorption in the visible region, it is preferred that the color of the dye would not substantially reside after image formation, and is preferred to employ a means for bleaching color by the heat of thermal development; in particular, it is preferred to add a thermal bleaching dye and a base precursor to the non-photosensitive layer to impart function as an antihalation layer. Those techniques are described in JP-A No. 11-231457 and the like.

[0329]

The amount of adding the thermal bleaching dye is determined depending on the usage of the dye. In general, it is used at an amount as such that the optical density (absorbance) exceeds 0.1 when measured at the desired wavelength. The optical density is preferably in the range from 0.15 to 2, and more preferably from 0.2 to 1. The addition amount of dyes to obtain optical

density in the above range is generally from 0.001 g/m² to 1 g/m².

[0330]

By thermal bleaching the dye in such a manner, the optical density after thermal development can be lowered to 0.1 or lower. Two types or more of thermal bleaching dyes may be used in combination in a photothermographic material. Similarly, two types or more of base precursors may be used in combination.

[0331]

In the case of thermal decolorization by the combined use of a decoloring dye and a base precursor, it is advantageous from the viewpoint of thermal decolorization efficiency to further use the substance capable of lowering the melting point by at least 3°C when mixed with the base precursor (e.g., diphenylsulfone, 4-chlorophenyl(phenyl)sulfone) as disclosed in JP-A No. 11-352626.

[0332]

3) Back layer

Back layers usable in the invention are described in paragraph Nos. 0128 to 0130 of JP-A No. 11-65021.

[0333]

In the invention, coloring matters having maximum absorption in the wavelength range of from 300 nm to 450 nm may be added in order to improve a

color tone of developed images and a deterioration of the images during aging. Such coloring matters are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, 01-61745, 2001-100363, and the like.

[0334]

Such coloring matters are generally added in the range from 0.1 mg/m² to 1 g/m², preferably to the back layer provided to the side opposite to the photosensitive layer.

[0335]

Further, in order to control the basic color tone, it is preferred to use a dye having an absorption peak in the wavelength range of from 580 nm to 680 nm. As a dye satisfying this purpose, preferred are oil-soluble azomethine dyes described in JP-A Nos. 4-359967 and 4-359968, or water-soluble phthalocyanine dyes described in Japanese Patent Application No. 2002-96797, which have low absorption intensity on the short wavelength side. The dyes for this purpose may be added to any of the layers, but more preferred is to add them in the non-photosensitive layer on the image forming surface side, or in the back surface side.

[0336]

The photothermographic material of the invention is preferably a so-called one-side photosensitive material, which comprises at least one layer of a photosensitive layer containing silver halide emulsion on one side of the support,

and a back layer on the other side.

[0337]

4) Matting agent

A matting agent may be preferably added to the photothermographic material of the invention in order to improve transportability. Description on the matting agent can be found in paragraphs Nos. 0126 to 0127 of JP-A No.11-65021. The amount of adding the matting agents is preferably in the range from 1 mg/m² to 400 mg/m², more preferably, from 5 mg/m² to 300 mg/m², with respect to the coating amount per m² of the photosensitive material.

[0338]

There is no particular restriction on the shape of the matting agent usable in the invention and it may have a fixed form or non-fixed form. Preferred is to use those having fixed form and globular shape. Average particle size is preferably in the range of from 0.5 μm to 10 μm, more preferably, from 1.0 μm to 8.0 μm, and most preferably, from 2.0 μm to 6.0 μm. Furthermore, the particle distribution of the matting agent is preferably set as such that the variation coefficient may become 50 % or lower, more preferably, 40 % or lower, and most preferably, 30 % or lower. The variation coefficient, herein, is defined by (the standard deviation of particle diameter)/(mean diameter of the particle) x 100. Furthermore, it is preferred to use by blending two types of matting agents having low variation coefficient and the ratio of their mean diameters is more than 3.

[0339]

The matness on the image forming layer surface is not restricted as far as star-dust trouble occurs, but the matness of 30 seconds to 2000 seconds is preferred, particularly preferred, 40 seconds to 1500 seconds as Beck's smoothness. Beck's smoothness can be calculated easily, by seeing Japan Industrial Standarded (JIS) P8119 "The method of testing Beck's smoothness for papers and sheets using Beck's test apparatus", or TAPPI standard method T479.

[0340]

The matt degree of the back layer in the invention is preferably in the range of 1200 seconds or less and 10 seconds or more; more preferably, 800 seconds or less and 20 seconds or more; and further preferably, 500 seconds or less and 40 seconds or more, as expressed by Beck smoothness.

[0341]

In the invention, the matting agent is incorporated preferably in the outermost surface layer on the photosensitive layer plane or a layer functioning as the outermost surface layer, or a layer near to the outer surface, and a layer that functions as the so-called protective layer.

[0342]

5) Polymer latex

In the case of the photothermographic material of the invention for graphic arts in which changing of dimension is critical, it is preferred to incorporate polymer latex in the surface protective layer and the back layer. As

such polymer latexes, descriptions can be found in “Gosei Jushi Emulsion (Synthetic resin emulsion)” (Taira Okuda and Hiroshi Inagaki, Eds., published by Kobunshi Kankokai (1978)), “Gosei Latex no Ouyou (Application of synthetic latex)” (Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki, and Keiji Kasahara, Eds., published by Kobunshi Kankokai (1993)), and “Gosei Latex no Kagaku (Chemistry of synthetic latex)” (Soichi Muroi, published by Kobunshi Kankokai (1970)). More specifically, there can be mentioned a latex of methyl methacrylate (33.5% by mass)/ethyl acrylate (50% by mass)/methacrylic acid (16.5% by mass) copolymer, a latex of methyl methacrylate (47.5% by mass)/butadiene (47.5% by mass)/itaconic acid (5% by mass) copolymer, a latex of ethyl acrylate/methacrylic acid copolymer, a latex of methyl methacrylate (58.9% by mass)/2-ethylhexyl methacrylate (25.4 % by mass)/styrene (8.6% by mass)/2-hydroethyl methacrylate (5.1% by mass)/acrylic acid copolymer, a latex of methyl methacrylate (64.0% by mass)/styrene (9.0% by mass)/butyl acrylate (20.0% by mass)/2-hydroxyethyl methacrylate(5.0% by mass)/acrylic acid copolymer, and the like. Furthermore, as the binder for the surface protective layer, there can be applied the the combinations of polymer latexes described in Japanese Patent Application No. 11-6872, the technology described in paragraph Nos. 0021 to 0025 of the specification of JP-A No. 2000-267226, technology described in paragraph Nos. 0027 and 0028 of the specification of Japanese Patent Application No. 11-6872, and the technology described in paragraph Nos. 0023 to 0041 of the specification of JP-A No. 2000-19678. The polymer latex in the surface protective layer preferably is contained in an amount of 10% by mass to 90% by mass, particularly preferably, of 20% by mass to 80% by mass of the total mass of binder.

[0343]

6) Surface pH

The surface pH of the photothermographic material according to the invention preferably yields a pH of 7.0 or lower, more preferably, 6.6 or lower, before thermal development treatment. Although there is no particular restriction concerning the lower limit, the pH value is about 3, and the most preferred surface pH range is from 4 to 6.2. From the viewpoint of reducing the surface pH, it is preferred to use an organic acid such as phthalic acid derivative or a non-volatile acid such as sulfuric acid, or a volatile base such as ammonia for the adjustment of the surface pH. In particular, ammonia can be used favorably for the achievement of low surface pH, because it can easily vaporize to remove it before the coating step or before applying thermal development.

It is also preferred to use a non-volatile base such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like, in combination with ammonia. The method of measuring surface pH value is described in paragraph No. 0123 of the specification of JP-A No. 2000-284399.

[0344]

7) Hardener

A hardener can be used in each of image forming layer, protective layer, back layer, and the like. As examples of the hardener, descriptions of various methods can be found in pages 77 to 87 of T.H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION" (Macmillan Publishing Co., Inc., 1977). Preferably used are, in addition to chromium alum, sodium salt of

2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide), and N,N-propylene bis(vinylsulfonacetamide), polyvalent metal ions described in page 78 of the above literature and the like, polyisocyanates described in USP No. 4281060, JP-A No. 6-208193 and the like, epoxy compounds of USP No. 4791042 and the like, and vinyl sulfone based compounds of JP-A No. 62-89048.

[0345]

The hardener is added as a solution, and the solution is added to the coating solution for forming the protective layer 180 minutes before coating to just before coating, preferably 60 minutes before to 10 seconds before coating. However, so long as the effect of the invention is sufficiently exhibited, there is no particular restriction concerning the mixing method and the conditions of mixing. As specific mixing methods, there can be mentioned a method of mixing in the tank, in which the average stay time calculated from the flow rate of addition and the feed rate to the coater is controlled to yield a desired time, or a method using static mixer as described in Chapter 8 of N. Harnby, M.F. Edwards, A.W. Nienow (translated by Koji Takahashi) "Liquid Mixing Technology" (Nikkan Kogyo Shinbun, 1989), and the like.

[0346]

8) Surfactant

As the surfactant, the solvent, the support, antistatic agent or the electrically conductive layer, and the method for obtaining color images applicable in the invention, there can be mentioned those disclosed in paragraph Nos. 0132, 0133, 0134, 0135, and 0136, respectively, of JP-A No. 11-65021. The

lubricant is described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and in paragraph Nos. 0049 to 0062 of Japanese Patent Application No. 11-106881.

[0347]

In the invention, preferably used are fluorocarbon surfactants. Specific examples of fluorocarbon surfactants can be found in those described in JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Polymer fluorocarbon surfactants described in JP-A 9-281636 can be also used preferably. For the photothermographic material in the invention, the fluorocarbon surfactants described in JP-A Nos. 2002-82411, Japanese Patent Application Nos. 2001-242357 and 2001-264110 are preferably used. Especially, the usage of the fluorocarbon surfactants described in Japanese Patent Application Nos. 2001-242357 and 2001-264110 in an aqueous coating solution is preferred viewed from the standpoint of capacity in static control, stability of the coating side state and sliding facility. The fluorocarbon surfactants described in Japanese Patent Application No. 2001-264110 is most preferred from the standpoint of capacity in static control, and small usage amount.

[0348]

According to the invention, the fluorocarbon surfactant can be used on either side of image forming layer side or back layer side, but is preferred to use on the both sides. Further, it is particularly preferred to use in combination with electrically conductive layer including aforementioned metal oxides. In this case the amount of the fluorocarbon surfactant on the side of the electrically conductive layer can be reduced or removed.

[0349]

The amount of the fluorocarbon surfactant used is preferably in the range from 0.1 mg/m² to 100 mg/m² on each side of image forming layer and back layer, more preferably 0.3 mg/m² to 30 mg/m², further preferably 1 mg/m² to 10 mg/m². The fluorocarbon surfactant described in Japanese Patent Application No. 2001-264110 has excellent effects, and is preferably used in the range from 0.01 mg/m² to 10 mg/m², and more preferably used in the range from 0.1 mg/m² to 5 mg/m².

[0350]

9) Antistatic agent

The photothermographic material of the invention preferably contains an electrically conductive layer including metal oxides or electrically conductive polymers. The antistatic layer may serve as an undercoat layer, or a back surface protective layer, and the like, but can also be placed specially. As an electrically conductive material of the antistatic layer, metal oxides having enhanced electric conductivity by the method of introducing oxygen defects or different types of metallic atoms into the metal oxides are preferably for use. Examples of metal oxides are preferably selected from ZnO, TiO₂ and SnO₂. As the combination of different types of atoms, preferred are ZnO combined with Al, In; SnO₂ with Sb, Nb, P, halogen atoms, and the like; TiO₂ with Nb, Ta, and the like; Particularly preferred for use is SnO₂ combined with Sb. The addition amount of different types of atoms is preferably in the range from 0.01 mol% to 30 mol%, and particularly preferably, in the range from 0.1 mol% to 10 mol%. The shape of the metal oxides can include, for example, spherical, needle-like, or

plate-like shape. The needle-like particles, with the ratio of (the major axis)/(the minor axis) is 2.0 or more, and more preferably, 3.0 to 50, is preferred viewed from the standpoint of the electric conductivity effect. The metal oxides is used preferably in the range from 1 mg/m² to 1000 mg/m², more preferably from 10 mg/m² to 500 mg/m², and further preferably from 20 mg/m² to 200 mg/m². The antistatic layer can be laid on either side of the image forming layer side or the back layer side, it is preferred to set between the support and the back layer. Examples of the antistatic layer in the invention include described in JP-A Nos. 11-65021, 56-143430, 56-143431, 58-62646, and 56-120519, and in paragraph Nos. 0040 to 0051 of JP-A No. 11-84573, US-P No. 5575957, and in paragraph Nos. 0078 to 0084 of JP-A No. 11-223898.

[0351]

10) Support

As the transparent support, favorably used is polyester, particularly, polyethylene terephthalate, which is subjected to heat treatment in the temperature range of from 130°C to 185°C in order to relax the internal strain caused by biaxial stretching and remaining inside the film, and to remove strain ascribed to heat shrinkage generated during thermal development. In the case of a photothermographic material for medical use, the transparent support may be colored with a blue dye (for instance, dye-1 described in the example of JP-A No. 8-240877), or may be uncolored. As to the support, it is preferred to apply undercoating technology, such as water-soluble polyester described in JP-A No. 11-84574, a styrene-butadiene copolymer described in JP-A No. 10-186565, a vinylidene chloride copolymer described in JP-A No. 2000-39684, and in the

paragraphs 0063 to 0080 of Japanese Patent Application No. 11-106881. The moisture content of the support is preferably 0.5% by weight or less when coating for image forming layer and back layer is conducted on the support.

[0352]

11) Other additives

Furthermore, antioxidant, stabilizing agent, plasticizer, UV absorbent, or a coating aid may be added to the photothermographic material. Each of the additives is added to either of the photosensitive layer or the non-photosensitive layer. Reference can be made to WO No. 98/36322, EP-A No. 803764A1, JP-A Nos. 10-186567 and 10-18568, and the like.

[0353]

12) Coating method

The photothermographic material of the invention may be coated by any method. More specifically, various types of coating operations inclusive of extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, or an extrusion coating using the type of hopper described in USP No. 2,681,294 are used. Preferably used is extrusion coating or slide coating described in pages 399 to 536 of Stephen F. Kistler and Peter M. Shweizer, "LIQUID FILM COATING" (Chapman & Hall, 1997), and most preferably used is slide coating. Example of the shape of the slide coater for use in slide coating is shown in Figure 11b.1, page 427, of the same literature. If desired, two or more layers can be coated simultaneously by the method described in pages 399 to 536 of the same literature, or by the method described in USP No. 2761791 and

British Patent No. 837095. Particularly preferred in the invention is the method described in JP-A Nos. 2001-194748, 2002-153808, 2002-153803, and 2002-182333.

[0354]

The coating solution for the layer containing organic silver salt in the invention is preferably a so-called thixotropic fluid. For the details of this technology, reference can be made to JP-A No. 11-52509. Viscosity of the coating solution for the layer containing organic silver salt in the invention at a shear velocity of 0.1S^{-1} is preferably from 400 mPa·s to 100,000 mPa·s, and more preferably, from 500 mPa·s to 20,000 mPa·s. At a shear velocity of 1000S^{-1} , the viscosity is preferably from 1 mPa·s to 200 mPa·s, and more preferably, from 5 mPa·s to 80 mPa·s.

[0355]

In the case of mixing two types of liquids on preparing the coating solution of the invention, known in-line mixer and in-plant mixer can be used favorably. Preferred in-line mixer of the invention is described in JP-A No. 2002-85948, and the in-plant mixer is described in JP-A No. 2002-90940.

[0356]

The coating solution of the invention is preferably subjected to defoaming treatment to maintain the coated surface in a fine state. Preferred defoaming treatment method in the invention is described in JP-A No. 2002-66431.

[0357]

In the case of applying the coating solution of the invention to the support, it is preferred to perform diselectrification in order to prevent the adhesion of dust, particulates, and the like due to charge up. Preferred example of the method of diselectrification for use in the invention is described in JP-A No. 2002-143747.

[0358]

Since a non-setting coating solution is used for the image forming layer in the invention, it is important to precisely control the drying wind and the drying temperature. Preferred drying method for use in the invention is described in detail in JP-A Nos. 2001-194749 and 2002-139814.

[0359]

In order to improve the film-forming properties in the photothermographic material of the invention, it is preferred to apply a heat treatment immediately after coating and drying. The temperature of the heat treatment is preferably in the range from 60°C to 100°C at the film surface, and heating time is preferably in the range from 1 second to 60 seconds. More preferably, the temperature of the heat treatment is in the range 70°C to 90°C at the film surface and heating time is 2 seconds to 10 seconds. A preferred method of heat treatment for the invention is described in JP-A No. 2002-107872.

[0360]

Furthermore, the production methods described in JP-A Nos. 2002-

156728 and 2002-182333 are favorably used in the invention in order to stably and continuously produce the photothermographic material of the invention.

[0361]

The photothermographic material is preferably of mono-sheet type (i.e., a type which can form image on the photothermographic material without using other sheets such as an image-receiving material).

[0362]

13) Wrapping material

In order to suppress fluctuation from occurring on the photographic property during a preservation of the photosensitive material of the invention before thermal development, or in order to improve curling or winding tendencies, it is preferred that a wrapping material having low oxygen transmittance and/or vapor transmittance is used. Preferably, oxygen transmittance is 50 mL·atm·m²·day or lower at 25°C, more preferably, 10 mL·atm·m²·day or lower, and most preferably, 1.0 mL·atm·m²·day or lower. Preferably, vapor transmittance is 10 g·atm·m²·day, more preferably, 5 g·atm·m²·day or lower, and most preferably, 1 g·atm·m²·day or lower.

[0363]

As specific examples of a wrapping material having low oxygen transmittance and/or vapor transmittance, reference can be made to, for instance, the wrapping material described in JP·A Nos.8-254793 and 2000-206653.

[0364]

14) Other applicable techniques

Techniques which can be used for the photothermographic material of the invention also include those in EP803764A1, EP883022A1, WO98/36322, JP-A Nos. 56-62648, 58-62644, JP-A Nos. 09-43766, 09-281637, 09-297367, 09-304869, 09-311405, 09-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, 11-343420, JP-A Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064 and 2000-171936.

[0365]

In instances of multi-color photothermographic materials, each photosensitive layer is in general, held distinctively each other by using a functional or nonfunctional barrier layer between each photosensitive layer as described in USP No. 4460681.

[0366]

Constitution of the multi-color photothermographic material may include a combination of these two layers for each color. Alternatively, all ingredients

may be included into a single layer as described in USP No. 4708928.

[0367]

2. Image forming method

In the present invention, a photothermographic material is exposed by an image recording apparatus and thermal developed, and thereby an image is formed on the material. The exposure to the material of the present invention is performed by a scanning exposure of laser beam. It is one of features of the image forming method used for the present invention that a distance from a scanning line of laser beam of the image recording apparatus to an insertion part of a thermal developing portion is 50 cm or less. The aforesaid scanning line indicates a position of scanning exposure with laser beam based on an image information data using a laser irradiation means at an orthogonal direction to a transport direction of a photothermographic material.

[0368]

2-1. Image recording apparatus

The image recording apparatus used for the image forming method of the present invention comprises a laser irradiation means to scan a laser beam based on an image data and to draw an image on the photothermographic materials, a transporting means to convey the exposed materials along the subscanning direction and to guide the materials to a thermal developing portion, and a thermal developing portion to develop the materials on heating. The thermal developing portion comprises an insertion part to accept the photothermographic materials, a heating part, and a carrying-out part to put the processed material

out of the thermal developing portion.

[0369]

For further understanding of the present invention, a specific embodiment of the image recording apparatus used for the present invention is illustrated in Fig.1, however the image recording apparatus used for the present invention is not particularly limited to the structure shown in Fig.1.

[0370]

The photothermographic material 11 is scan-exposed by the laser irradiation means 20 with laser beam B based on an image data at an orthogonal direction to the transportation direction of the material, while it is conveyed by driving rollers 17A, 17B. Thereafter, the exposed material is successively conveyed and inserted to the thermal developing portion 34 through the guide portion 32.

The thermal developing portion 34 comprises three sheets of heating plates 40, a plurality of press rollers 42 to contact the photothermographic material to the heating plates, and a casing 36 to cover all of the thermal developing portion. The photothermographic material after passing through the thermal developing portion is carried out and then cooled down to a stable temperature region through a cooling zone, thereafter the processed material is carried out from the apparatus.

In the case of the image recording apparatus 10 shown in Fig.1, as for the distance from the laser exposing portion to the thermal developing portion in the present invention, the distance from the point 18 of scanning exposure in the

photothermographic material 11 to the insertion part of the thermal developing portion (in Fig.1, the opening end of the casing where the photothermographic material is inserted) is 50 cm or less.

[0371]

By the image forming method that make the distance from a scanning line of laser exposing portion to a thermal developing portion to be 50 cm or less, and using the above-mentioned photothermographic material, the size of image recording apparatus can be reduced.

The above-mentioned distance is preferably 45 cm or less, and more preferably 40 cm or less. There is no lower limit for the said distance, if the apparatus construction is available. However it is not desirable that the guide plate 16 of laser exposing portion is disposed directly to the casing 36 or the heating plates 40, because the heat of the heating portion would conduct to the laser exposing portion.

[0372]

The image forming method using the forming apparatus of the invention exhibits preferred characteristics when used together with a thermal developing apparatus that is configured for rapid process described later.

[0373]

2-2. Exposure

As laser beam according to the invention, He-Ne laser of red through infrared emission, red laser diode, or Ar⁺, He-Ne, He-Cd laser of blue through

green emission, blue laser diode are used. Preferred laser is red to infrared laser diode and the peak wavelength of laser beam is 600 nm to 900 nm, preferably 620 nm to 850 nm. In recent years, development has been made particularly on a light source module with an SHG (a second harmonic generator) and a laser diode integrated into a single piece whereby a laser output apparatus in a short wavelength region has come into the limelight. A blue laser diode enables high definition image recording and makes it possible to obtain an increase in recording density and a stable output over a long lifetime, which results in expectation of an expanded demand in the future. The peak wavelength of blue laser beam is preferably 300 nm to 500 nm, and more preferably 400 nm to 500 nm.

Laser beam which oscillates in a longitudinal multiple modulation by a method such as high frequency superposition is also preferably employed.

[0374]

2-3. Thermal development

Although the development of the photothermographic material of the invention is usually performed by elevating the temperature of the photothermographic material exposed imagewise, any method may be used for this thermal development process. The temperature for the development is preferably 80°C to 250°C, preferably 100°C to 140°C, and more preferably 110°C to 130°C.

Time period for the development is preferably 6 seconds to 14 seconds, from viewpoints of the productivity and the stability of photographic performances, more preferably from 7 seconds to 13 seconds, and still more

preferably from 8 seconds to 12 seconds.

[0375]

According to the process for the thermal development, either drum type heaters or plate type heaters may be used.

Preferable process for the thermal development by a plate type heater may be a process described in JP-A No. 11-133572, which discloses a thermal developing apparatus in which a visible image is obtained by bringing a photothermographic material with a formed latent image into contact with a heating means at a thermal development portion, wherein the heating means comprises a plate heater, and plurality of press rollers are oppositely provided along one surface of the plate heater, the thermal developing apparatus is characterized in that thermal development is performed by passing the photothermographic material between the press rollers and the plate heater. It is preferred that the plate heater is divided into 2 to 6 portions, with the leading end having the lower temperature by 1°C to 10°C. For example, four stages of plate heaters which can be independently subjected to the temperature control are used, and are controlled so that they respectively become 112°C, 119°C, 121°C, and 120°C. Such a process is also described in JP-A No. 54-30032, which allows for excluding moisture and organic solvents included in the photothermographic material out of the system, and also allows for suppressing the change of shapes of the support of the photothermographic material upon rapid heating of the photothermographic material.

[0376]

In order to reduce the size of thermal developing apparatus and shorten the thermal development time, a stable temperature control of heaters is required. It is still another feature of the present invention that the leading part of the exposed sheet is started to thermal development while the last part of the sheet is still subjected to exposure. Preferred examples of the imager suitable for the rapid processing of the photothermographic material of the present invention are described in Japanese Patent Application Nos. 2001-088832 and 2001-091114. With the imager equipped with the said plate type heaters where the temperatures of three stages of the heaters are controlled to 107°C, 121°C, and 121°C respectively, the thermal development of the material is performed within 14 seconds. And therefore the output time of the first sheet can be reduced to about 60 seconds. In order to perform such a rapid development processing, it is preferred to use the photothermographic materials of the present invention having a high sensitivity and stability to the environmental temperature.

[0377]

2-4. System

Examples of a medical laser imager equipped with a light exposing portion and a thermal developing portion include Fuji Medical Dry Laser Imager FM-DP L and DRYPIX 7000. In connection with FM-DP L, description is found in Fuji Medical Review No. 8, pages 39 to 55. It goes without mentioning that those techniques may be applied as the laser imager for the photothermographic material of the invention. In addition, the present photothermographic material can be also applied as a photothermographic material for the laser imager used

in "AD network" which was proposed by Fuji Film Medical Co., Ltd. as a network system accommodated to DICOM standard.

[0378]

3. Application of the invention

The image forming method in which the photothermographic material of the invention is used is preferably employed as image forming methods for photothermographic materials for use in medical imaging, photothermographic materials for use in industrial photographs, photothermographic materials for use in graphic arts, as well as for COM, through forming black and white images by silver imaging.

[0379]

[Examples]

The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

Example 1

[0380]

(Preparation of PET Support)

1) Film Manufacturing

PET having IV (intrinsic viscosity) of 0.66 (measured in phenol/tetrachloroethane = 6/4 (mass ratio) at 25°C) was obtained according to a conventional manner using terephthalic acid and ethylene glycol. The product was pelletized, dried at 130°C for 4 hours, melted at 300°C. Thereafter, the

mixture was extruded from a T-die and rapidly cooled to form a non-tentered film having such a thickness that the thickness should become 175 μm after tentered and thermal fixation.

[0381]

The film was stretched along the longitudinal direction by 3.3 times using rollers of different peripheral speeds, and then stretched along the transverse direction by 4.5 times using a tenter machine. The temperatures used for these operations were 110°C and 130°C, respectively. Then, the film was subjected to thermal fixation at 240°C for 20 seconds, and relaxed by 4% along the transverse direction at the same temperature. Thereafter, the chucking part was slit off, and both edges of the film were knurled. Then the film was rolled up at the tension of 4 kg/cm² to obtain a roll having the thickness of 175 μm .

[0382]

2) Surface Corona Discharge Treatment

Both surfaces of the support were treated at room temperature at 20 m/minute using Solid State Corona Discharge Treatment Machine Model 6KVA manufactured by Piller GmbH. It was proven that treatment of 0.375 kV · A minute/m² was executed, judging from the readings of current and voltage on that occasion. The frequency upon this treatment was 9.6 kHz, and the gap clearance between the electrode and dielectric roll was 1.6 mm.

[0383]

3) Undercoating

〈Preparations of Coating Solution for Undercoat Layer〉

Formula (1) (for undercoat layer on the image forming layer side)

Pesresin A-520 manufactured by Takamatsu Oil & Fat Co., Ltd. (30% by mass solution) 59 g

polyethyleneglycol monononylphenylether (average ethylene oxide number = 8.5) 10% by mass solution 5.4 g

MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd. (polymer fine particle, mean particle diameter of 0.4 μm) 0.91 g

distilled water 935 mL

[0384]

Formula (2) (for first layer on the back surface)

Styrene-butadiene copolymer latex (solid content of 40% by mass, styrene/butadiene mass ratio = 68/32) 158 g

8% by mass aqueous solution of 2,4-dichloro-6-hydroxy-S-triazine sodium salt 20 g

1% by mass aqueous solution of sodium laurylbenzenesulfonate

10 mL

distilled water 854 mL

[0385]

Formula (3) (for second layer on the back surface)

SnO₂/SbO (9/1 mass ratio, mean particle diameter of 0.038 μm , 17% by mass dispersion) 84 g

gelatin (10% by mass aqueous solution) 89.2 g

METOLOSE TC-5 manufactured by Shin-Etsu Chemical Co., Ltd. (2% by mass aqueous solution)	8.6 g
MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd.	0.01 g
1% by mass aqueous solution of sodium dodecylbenzenesulfonate	10 mL
NaOH (1% by mass)	6 mL
Proxel (manufactured by Imperial Chemical Industries PLC)	1 mL
distilled water	805 mL

[0386]

⟨Undercoating⟩

Both surfaces of the biaxially tentered polyethylene terephthalate support having the thickness of 175 μm were subjected to the corona discharge treatment as described above. Thereafter, the aforementioned formula (1) of the coating solution for the undercoat was coated on one surface (image forming layer side) with a wire bar so that the amount of wet coating became 6.6 mL/m^2 (per one side), and dried at 180°C for 5 minutes. Then, the aforementioned formula (2) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 5.7 mL/m^2 , and dried at 180°C for 5 minutes. Furthermore, the aforementioned formula (3) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 7.7 mL/m^2 , and dried at 180°C for 6 minutes. Thus, an undercoated support was produced.

[0387]

(Back Layer)

1) Preparations of coating solution for back layer

⟨Preparation of Dispersion of Solid Fine Particles (a) of Base Precursor⟩

A base precursor compound-1 in an amount of 2.5 kg, and 300 g of a surfactant (trade name: DEMOL N, manufactured by Kao Corporation), 800 g of diphenyl sulfone, 1.0 g of benzoisothiazolinone sodium salt and distilled water were added to give the total amount of 8.0 kg and mixed. The mixed liquid was subjected to beads dispersion using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.). Process for dispersion included feeding the mixed liquid to UVM-2 packed with zirconia beads having the mean particle diameter of 0.5 mm with a diaphragm pump, followed by the dispersion at the inner pressure of 50 hPa or higher until desired mean particle diameter could be achieved.

[0388]

The dispersion was continued until the ratio of the optical density at 450 nm and the optical density at 650 nm for the spectral absorption of the dispersion (D450/D650) became 3.0 upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the base precursor became 25% by mass, and filtrated (with a polypropylene filter having the mean fine pore diameter of 3 μm) for eliminating dust to put into practical use.

[0389]

⟨Preparation of Dispersion of Solid Fine Particle of Dye⟩

A cyanine dye compound-1 in an amount of 6.0 kg, and 3.0 kg of sodium p-dodecylbenzenesulfonate, 0.6 kg of DEMOL SNB (a surfactant manufactured by Kao Corporation), and 0.15 kg of a defoaming agent (trade name: SURFYNOL 104E, manufactured by Nissin Chemical Industry Co., Ltd.) were mixed with distilled water to give the total liquid amount of 60 kg. The mixed liquid was subjected to dispersion with 0.5 mm zirconia beads using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.).

[0390]

The dispersion was dispersed until the ratio of the optical density at 650 nm and the optical density at 750 nm for the spectral absorption of the dispersion (D650/D750) became 5.0 or more upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the cyanine dye became 6% by mass, and filtrated with a filter (mean fine pore diameter: 1 μm) for eliminating dust to put into practical use.

[0391]

⟨Preparation of Coating Solution for Antihalation Layer⟩

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 20 g of monodispersed polymethyl methacrylate fine particles (mean particle size of 8 μm , standard deviation of particle diameter of 0.4), 0.1 g of benzoisothiazolinone and 490 mL of water to allow gelatin to be dissolved. Additionally, 2.3 mL of a 1 mol/L aqueous sodium hydroxide solution, 40 g of the aforementioned dispersion

of the solid fine particle of the dye, 90 g of the aforementioned dispersion of the solid fine particles (a) of the base precursor, 12 mL of a 3% by mass aqueous solution of sodium polystyrenesulfonate, and 180 g of a 10% by mass solution of SBR latex were admixed. Just prior to the coating, 80 mL of a 4% by mass aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the antihalation layer.

[0392]

⟨Preparation of Coating Solution for Back Surface Protective Layer⟩

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 35 mg of benzoisothiazolinone and 840 mL of water to allow gelatin to be dissolved. Additionally, 5.8 mL of a 1 mol/L aqueous sodium hydroxide solution, liquid paraffin emulsion at 1.5 g equivalent to liquid paraffin, 10 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 20 mL of a 3% by mass aqueous solution of sodium polystyrenesulfonate, 2.4 mL of a 2% by mass solution of a fluorocarbon surfactant (F-1), 2.4 mL of a 2% by mass solution of another fluorocarbon surfactant (F-2), and 32 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (copolymer mass ratio of 57/8/28/5/2) latex were admixed. Just prior to the coating, 25 mL of a 4% by mass aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the back surface protective layer.

[0393]

2) Coating of Back Layer

The back surface side of the undercoated support as described above was subjected to simultaneous double coating so that the coating solution for the antihalation layer gives the coating amount of gelatin of 0.52 g/m², and so that the coating solution for the back surface protective layer gives the coating amount of gelatin of 1.7 g/m², followed by drying to produce a back layer.

[0394]

(Image Forming Layer, Intermediate Layer, and Surface Protective Layer)

1. Preparations of Materials for Coating

1) Silver Halide Emulsion

<<Preparation of Silver Halide Emulsion-1>>

To 1421 mL of distilled water was added 3.1 mL of a 1% by mass potassium bromide solution. Further, a liquid added with 3.5 mL of sulfuric acid having the concentration of 0.5 mol/L and 31.7 g of phthalated gelatin was kept at 30°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 95.4 mL; and solution B prepared through diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with distilled water to give the volume of 97.4 mL, over 45 seconds at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added. Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 44.2 g of potassium

bromide and 2.2 g of potassium iodide with distilled water to give the volume of 400 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 20 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1. Hexachloroiridium (III) potassium salt was added to give 1×10^{-4} mol per one mol of silver at 10 minutes post initiation of the addition of the solution C and the solution D in its entirety. Moreover, at 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added at a total amount of 3×10^{-4} mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with sulfuric acid at the concentration of 0.5 mol/L. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with sodium hydroxide at the concentration of 1 mol/L to produce a silver halide dispersion having the pAg of 8.0.

[0395]

The silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzoisothiazoline-3-one, followed by elevating the temperature to 47°C at 40 minutes thereafter. At 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added at 7.6×10^{-5} mol per one mol of silver. At additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added at 2.9×10^{-4} mol per one mol of silver and subjected to aging for 91 minutes. Thereafter, a methanol solution of a spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 was added thereto at 1.2×10^{-3} mol in total of the

spectral sensitizer A and B per one mol of silver. At one minute later, 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N",N"-diethylmelamine in methanol was added thereto, and at additional 4 minutes thereafter, 5-methyl-2-mercaptopbenzimidazole in a methanol solution at 4.8×10^{-3} mol per one mol of silver, 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole in a methanol solution at 5.4×10^{-3} mol per one mol of silver, and 1-(3-methylureidophenyl)-5-mercaptotetrazole in an aqueous solution at 8.5×10^{-3} mol per one mol of silver were added to produce a silver halide emulsion-1.

[0396]

Grains in thus prepared silver halide emulsion were silver iodobromide grains having a mean sphere equivalent diameter of 0.042 μm , a variation coefficient of 20%, which uniformly include iodine at 3.5 mol%. Grain size and the like were determined from the average of 1000 grains using an electron microscope. The [100] face ratio of this grain was found to be 80% using a Kubelka-Munk method.

[0397]

<<Preparation of Silver Halide Emulsion-2>>

Preparation of silver halide emulsion-2 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-1 except that: the temperature of the liquid upon the grain formation step was altered from 30°C to 47°C; the solution B was changed to that prepared through diluting 15.9 g of potassium bromide with distilled water to give the volume of 97.4 mL; the solution D was changed to that prepared through diluting 45.8 g of potassium

bromide with distilled water to give the volume of 400 mL; time period for adding the solution C was changed to 30minutes; and potassium iron (II) hexacyanide was deleted. The precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Furthermore, the spectral sensitization, chemical sensitization, and addition of 5-methyl-2-mercaptopbenzimidazole and 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole was executed similarly to the emulsion-1 except that: the amount of the tellurium sensitizer C to be added was changed to 1.1×10^{-4} mol per one mol of silver; the amount of the methanol solution of the spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 to be added was changed to 7.0×10^{-4} mol in total of the spectral sensitizer A and the spectral sensitizer B per one mol of silver; the addition of 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole was changed to give 3.3×10^{-3} mol per one mol of silver; and the addition of 1-(3-methylureidophenyl)-5-mercaptotetrazole was changed to give 4.7×10^{-3} mol per one mol of silver to produce a silver halide emulsion-2. The emulsion grains in the silver halide emulsion-2 were pure cubic silver bromide grains having a mean sphere equivalent diameter of 0.080 μm and a variation coefficient of 20%.

[0398]

<<Preparation of Silver Halide Emulsion-3>>

Preparation of a silver halide emulsion-3 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-1 except that the temperature of the liquid upon the grain formation step was altered from 30°C to 27°C. In addition, the precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Silver

halide emulsion-3 was obtained similarly to the emulsion-1 except that: the addition of the methanol solution of the spectral sensitizer A and the spectral sensitizer B was changed to the solid dispersion (aqueous gelatin solution) at a molar ratio of 1 : 1 with the amount to be added being 6.0×10^{-3} mol in total of the spectral sensitizer A and spectral sensitizer B per one mol of silver; the amount of the tellurium sensitizer C to be added was changed to 5.2×10^{-4} mol per one mol of silver; and bromoauric acid at 5×10^{-4} mol per one mol of silver and potassium thiocyanate at 2×10^{-3} mol per one mol of silver were added at 3 minutes following the addition of the tellurium sensitizer. The grains in the silver halide emulsion-3 were silver iodobromide grains having a mean sphere equivalent diameter of $0.034 \mu\text{m}$ and a variation coefficient of 20%, which uniformly include iodine at 3.5 mol%.

[0399]

<<Preparation of Mixed Emulsion A for Coating Solution>>

The silver halide emulsion-1 at 70% by mass, the silver halide emulsion-2 at 15% by mass and the silver halide emulsion-3 at 15% by mass were dissolved, and thereto was added benzothiazolium iodide at 7×10^{-3} mol per one mol of silver with a 1% by mass aqueous solution. Further, water was added thereto to give the content of silver of 38.2 g per one kg of the mixed emulsion for a coating solution, and 1-(3-methylureidophenyl)-5-mercaptotetrazole was added to give 0.34 g per 1 kg of the mixed emulsion for a coating solution.

[0400]

Further, as "a compound that can be one-electron-oxidized to provide a

one-electron oxidation product, which releases one or more electrons", the compounds Nos. 1, 20 and 26 were added respectively in an amount of 2×10^{-3} mol per one mol of silver halide.

[0401]

2) Preparations of Dispersion of Silver Salt of Fatty Acid

《Dispersion of Silver Salt of Fatty Acid A》

87.6 kg of behenic acid (Henkel Co., trade name: Edenor C22-85R), 423 L of distilled water, 49.2 L of an aqueous sodium hydroxide solution at the concentration of 5 mol/L, 120 L of t-butyl alcohol were admixed, and subjected to a reaction with stirring at 75°C for one hour to give a solution of a sodium behenate A. Separately, 206.2 L of an aqueous solution of 40.4 kg of silver nitrate (pH 4.0) was provided, and kept at a temperature of 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was kept at 30°C, and thereto were added the total amount of the solution of a sodium behenate A and the total amount of the aqueous silver nitrate solution with sufficient stirring at a constant flow rate over 93 minutes and 15 seconds, and 90 minutes, respectively. Upon this operation, during first 11 minutes following the initiation of adding the aqueous silver nitrate solution, the added material was restricted to the aqueous silver nitrate solution alone. The addition of the solution of a sodium behenate A was thereafter started, and during 14 minutes and 15 seconds following the completion of adding the aqueous silver nitrate solution, the added material was restricted to the solution of a sodium behenate A alone. The temperature inside of the reaction vessel was then set to be 30°C, and the temperature outside was controlled so that the liquid temperature could

be kept constant. In addition, the temperature of a pipeline for the addition system of the solution of a sodium behenate A was kept constant by circulation of warm water outside of a double wall pipe, so that the temperature of the liquid at an outlet in the leading edge of the nozzle for addition was adjusted to be 75°C. Further, the temperature of a pipeline for the addition system of the aqueous silver nitrate solution was kept constant by circulation of cool water outside of a double wall pipe. Position at which the solution of a sodium behenate A was added and the position at which the aqueous silver nitrate solution was added were arranged symmetrically with a shaft for stirring located at a center. Moreover, both of the positions were adjusted to avoid contact with the reaction liquid.

[0402]

After completing the addition of the solution of a sodium behenate A, the mixture was left to stand at the temperature as it is for 20 minutes. The temperature of the mixture was then elevated to 35°C over 30 minutes followed by aging for 210 minutes. Immediately after completing the aging, solid matters were filtered out with centrifugal filtration. The solid matters were washed with water until the electric conductivity of the filtrated water became 30 μ S/cm. A silver salt of fatty acid was thus obtained. The resulting solid matters were stored as a wet cake without drying.

[0403]

When the shape of the resulting particles of the silver behenate was evaluated by an electron micrography, a flake crystal was revealed having a =

0.14 μm , $b = 0.4 \mu\text{m}$ and $c = 0.6 \mu\text{m}$ on the average value, with a mean aspect ratio of 5.2, a mean sphere equivalent diameter of 0.52 μm and a variation coefficient of 15% (a, b and c are as defined aforementioned.).

[0404]

To the wet cake corresponding to 260 kg of a dry solid matter content, were added 19.3 kg of polyvinyl alcohol (trade name: PVA-217) and water to give the total amount of 1000 kg. Then, slurry was obtained from the mixture using a dissolver blade. Additionally, the slurry was subjected to preliminary dispersion with a pipeline mixer (manufactured by MIZUHO Industrial Co., Ltd.: PM-10 type).

[0405]

Next, a stock liquid after the preliminary dispersion was treated three times using a dispersing machine (trade name: Microfluidizer M-610, manufactured by Microfluidex International Corporation, using Z type Interaction Chamber) with the pressure controlled to be 1260 kg/cm² to give a dispersion of the silver behenate (a dispersion of silver salt of fatty acid). For the cooling manipulation, coiled heat exchangers were equipped before and after of the interaction chamber respectively, and accordingly, the temperature for the dispersion was set to be 18°C by regulating the temperature of the cooling medium.

[0406]

3) Preparations of Reducing Agent Dispersion

<<Preparation of Reducing Agent-1 Dispersion>>

To 10 kg of a reducing agent-1 (2,2'-methylenebis-(4-ethyl-6-tert-butylphenol)) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by mass. This dispersion was subjected to thermal treatment at 60°C for 5 hours to obtain a reducing agent-1 dispersion. Particles of the reducing agent included in the resulting reducing agent dispersion had a median diameter of 0.40 μm , and a maximum particle diameter of 1.4 μm or less. The resultant reducing agent dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

[0407]

<<Preparation of Reducing Agent-2 Dispersion>>

To 10 kg of a reducing agent-2 (6,6'-di-t-butyl-4,4'-dimethyl-2,2'-butylienediphenol)) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the

mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a reducing agent-2 dispersion. Particles of the reducing agent included in the resulting reducing agent-2 dispersion had a median diameter of 0.50 µm, and a maximum particle diameter of 1.6 µm or less. The resultant reducing agent-2 dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and stored.

[0408]

4) Preparation of Hydrogen Bonding Compound-1 Dispersion

To 10 kg of a hydrogen bonding compound-1 (tri(4-t-butylphenyl)phosphineoxide) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 4 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the hydrogen bonding compound to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a hydrogen bonding compound-1 dispersion. Particles of the hydrogen bonding compound included

in the resulting hydrogen bonding compound dispersion had a median diameter of 0.45 μm , and a maximum particle diameter of 1.3 μm or less. The resultant hydrogen bonding compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

[0409]

5) Preparation of Development Accelerator-1 Dispersion

To 10 kg of a development accelerator-1 and 20 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the development accelerating agent to be 20% by mass. Accordingly, a development accelerator-1 dispersion was obtained. Particles of the development accelerator included in the resulting development accelerator dispersion had a median diameter of 0.48 μm , and a maximum particle diameter of 1.4 μm or less. The resultant development accelerator dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

[0410]

6) Preparations of Organic Polyhalogen Compound Dispersion

《Preparation of Organic Polyhalogen Compound-1 Dispersion》

An organic polyhalogen compound-1 (compound No. 1a-1 of formula (1a)) in an amount of 10 kg, 10 kg of a 20% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203), 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalenesulfonate and 14 kg of water were added, and thoroughly admixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 26% by mass. Accordingly, an organic polyhalogen compound-1 dispersion was obtained. Particles of the organic polyhalogen compound included in the resulting organic polyhalogen compound dispersion had a median diameter of 0.41 μm , and a maximum particle diameter of 2.0 μm or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 10.0 μm to remove foreign substances such as dust, and stored.

[0411]

《Preparation of Organic Polyhalogen Compound-2 Dispersion》

Preparation of organic polyhalogen compound-2 dispersion was conducted in a similar manner to the preparation of organic polyhalogen compound-1 dispersion except that using organic polyhalogen compound-2 (compound No. 1b-

30 of formula (1b)) instead of using organic polyhalogen compound-1.

[0412]

«Preparation of Organic Polyhalogen Compound-3 Dispersion»

Preparation of organic polyhalogen compound-3 dispersion was conducted in a similar manner to the preparation of organic polyhalogen compound-1 dispersion except that using organic polyhalogen compound-3 (compound No. 1c-1 of formula (1c)) instead of using organic polyhalogen compound-1.

[0413]

«Preparations of Comparative Dispersion of Organic Polyhalogen Compound-4»

For comparison, preparation of organic polyhalogen compound-4 dispersion was conducted in a similar manner to the preparation of organic polyhalogen compound-1 dispersion except that using organic polyhalogen compound-4 (tribromomethane sulfonylbenzene) instead of using organic polyhalogen compound-1.

[0414]

7) Preparation of Phthalazine Compound-1 Solution

Modified polyvinyl alcohol MP203 in an amount of 8 kg was dissolved in 174.57 kg of water, and then thereto were added 3.15 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalenesulfonate and 14.28 kg of a 70% by mass aqueous solution of phthalazine compound-1 (6-isopropyl phthalazine) to prepare a 5% by mass phthalazine compound-1 solution.

[0415]

8) Preparations of Mercapto Compound Solution

《Preparation of an Aqueous Solution of Mercapto Compound-1》

A mercapto compound-1 (1-(3-sulfophenyl)-5-mercaptotetrazole sodium salt) in an amount of 7 g was dissolved in 993 g of water to give a 0.7% by mass aqueous solution.

[0416]

《Preparation of an Aqueous Solution of Mercapto Compound-2》

A mercapto compound-2 (1-(3-methylureidophenyl)-5-mercaptotetrazole) in an amount of 20 g was dissolved in 980 g of water to give a 2.0% by mass aqueous solution.

[0417]

9) Preparation of Pigment-1 Dispersion

C.I. Pigment Blue 60 in an amount of 64 g and 6.4 g of DEMOL N manufactured by Kao Corporation were added to 250 g water and thoroughly mixed to give slurry. Zirconia beads having the mean particle diameter of 0.5 mm were provided in an amount of 800 g, and charged in a vessel with the slurry. Dispersion was performed with a dispersing machine (1/4G sand grinder mill: manufactured by IMEX Co., Ltd.) for 25 hours. Thereto was added water to adjust so that the concentration of the pigment became 5% by mass to obtain a pigment-1 dispersion. Particles of the pigment included in the resulting pigment dispersion had a mean particle diameter of 0.21 μm .

[0418]

10) Preparation of SBR Latex Solution

To a polymerization tank of a gas monomer reaction apparatus (manufactured by Taiatsu Techno Corporation, TAS-2J type), were charged 287 g of distilled water, 7.73 g of a surface active agent (Pionin A-43-S (manufactured by TAKEMOTO OIL & FAT CO., LTD.): solid matter content of 48.5% by mass), 14.06 mL of 1 mol/L sodium hydroxide, 0.15 g of ethylenediamine tetraacetate tetrasodium salt, 255 g of styrene, 11.25 g of acrylic acid, and 3.0 g of tert-dodecyl mercaptan, followed by sealing of the reaction vessel and stirring at a stirring rate of 200 rpm. Degassing was conducted with a vacuum pump, followed by repeating nitrogen gas replacement several times. Thereto was injected 108.75 g of 1,3-butadiene, and the inner temperature was elevated to 60°C. Thereto was added a solution of 1.875 g of ammonium persulfate dissolved in 50 mL of water, and the mixture was stirred for 5 hours as it stands. The temperature was further elevated to 90°C, followed by stirring for 3 hours. After completing the reaction, the inner temperature was lowered to reach to the room temperature, and thereafter the mixture was treated by adding 1 mol/L sodium hydroxide and ammonium hydroxide to give the molar ration of Na^+ ion : NH_4^+ ion = 1 : 5.3, and thus, the pH of the mixture was adjusted to 8.4. Thereafter, filtration with a polypropylene filter having the pore size of 1.0 μm was conducted to remove foreign substances such as dust followed by storage. Accordingly, SBR latex was obtained in an amount of 774.7 g. Upon the measurement of halogen ion by ion chromatography, concentration of chloride ion was revealed to be 3 ppm. As a result of the measurement of the concentration of the chelating agent by high

performance liquid chromatography, it was revealed to be 145 ppm.

[0419]

The aforementioned latex had the mean particle diameter of 90 nm, Tg of 17°C, solid matter concentration of 44% by mass, the equilibrium moisture content at 25°C, 60% RH of 0.6% by mass, ionic conductance of 4.80 mS/cm (measurement of the ionic conductance performed using a conductivity meter CM-30S manufactured by Toa Electronics Ltd. for the latex stock solution (44% by mass) at 25°C).

[0420]

2. Preparations of Coating Solutions

1) Preparations of Coating Solution for Image Forming Layer-1 to -4

The dispersion of the silver salt of fatty acid obtained as described above in an amount of 1000 g, 135 mL of water, 35 g of the pigment-1 dispersion, dispersion of organic polyhalogen compound-1 to -4 (shown in Table 1), 162 g of the phthalazine compound-1 solution, 1060 g of the SBR latex (Tg: 17°C) solution, 75 g of the reducing agent-1 dispersion, 75 g of the reducing agent-2 dispersion, 106 g of the hydrogen bonding compound-1 dispersion, 19.2 g of the development accelerator-1 dispersion, 18 mL of the mercapto compound-1 aqueous solution and 45 mL of the mercapto compound-2 aqueous solution were serially added. The coating solution for the image forming layer prepared by adding 118 g of the mixed emulsion A for coating solution thereto followed by thorough mixing just prior to the coating was fed directly to a coating die, and was coated.

[0421]

The amount of zirconium in the coating solution was 0.32 mg per g of silver.

[0422]

2) Coating Solution for Intermediate Layer

To 1000 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 163 g of the pigment-1 dispersion, 33g of an aqueous solution of a blue dye-1 (manufactured by Nippon Kayaku Co., Ltd.: Kayafect turquoise RN liquid 150), 27 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate and 4200 mL of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (mass ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, were added 27 mL of a 5% by mass aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 135 mL of a 20% by mass aqueous solution of ammonium secondary phthalate and water to give total amount of 10000 g. The mixture was adjusted with NaOH to give the pH of 7.5. Accordingly, the coating solution for the intermediate layer was prepared, and was fed to a coating die to provide 8.9 mL/m².

[0423]

Viscosity of the coating solution was 58 [mPa s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0424]

3) Coating Solution for First Layer of Surface Protective Layers

In 840 mL of water were dissolved 100 g of inert gelatin and 10 mg of benzoisothiazolinone, and thereto were added 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (mass ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 46 mL of a 15% by mass methanol solution of phthalic acid and 5.4 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, and were mixed. Immediately before coating, 40 mL of a 4% by mass chrome alum which had been mixed with a static mixer was fed to a coating die so that the amount of the coating solution became 26.1 mL/m².

Viscosity of the coating solution was 20 [mPa s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0425]

4) Coating Solution for Second Layer of Surface Protective Layers

In 800 mL of water were dissolved 100 g of inert gelatin and 10 mg of benzoisothiazolinone, and thereto were added liquid paraffin emulsion at 8.0 g equivalent to liquid paraffin, 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (mass ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 40 mL of a 15% by mass methanol solution of phthalic acid, 5.5 mL of a 1% by mass solution of a fluorocarbon surfactant (F-1), 5.5 mL of a 1% by mass aqueous solution of another fluorocarbon surfactant (F-2), 28 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 4 g of polymethyl methacrylate fine particles (mean particle diameter of 0.7 µm) and 21 g of polymethyl methacrylate fine particles (mean particle diameter of 4.5 µm), and were mixed to give a

coating solution for the surface protective layer, which was fed to a coating die so that 8.3 mL/m² could be provided.

[0426]

Viscosity of the coating solution was 19 [mPa · s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0427]

3) Preparations of Photothermographic Material-1 to -4

Reverse surface of the back surface was subjected to simultaneous overlaying coating by a slide bead coating method in order of the image forming layer, intermediate layer, first layer of the surface protective layers and second layer of the surface protective layers starting from the undercoated face, and thus a sample of the photothermographic material was produced. In this method, the temperature of the coating solution was adjusted to 31°C for the image forming layer and intermediate layer, to 36°C for the first layer of the surface protective layers, and to 37°C for the second layer of the surface protective layers.

[0428]

The coating amount of each compound for the image forming layer (g/m²) is as follows.

[0429]

Silver salt of fatty acid (on the basis of Ag content)	1.31
Pigment-1 (C. I. Pigment Blue 60)	0.036

Organic polyhalogen compound (see Table 1)	0.25
Phthalazine compound-1	0.18
SBR latex	9.70
Reducing agent-1	0.40
Reducing agent-2	0.40
Hydrogen bonding compound-1	0.58
Development accelerator-1	0.08
Mercapto compound-1	0.004
Mercapto compound-2	0.020
Silver halide (on the basis of Ag content)	0.10

[0430]

Conditions for coating and drying are as follows.

Coating was performed at the speed of 160 m/min, with the clearance between the leading end of the coating die and the support being 0.10 mm to 0.30 mm, and with the pressure in the vacuum chamber set to be lower than atmospheric pressure by 196 Pa to 882 Pa. The support was discharged by ionic wind prior to coating.

In the subsequent cooling zone, the coating solution was cooled by wind having the dry-bulb temperature of 10°C to 20°C. Thereafter, conveyance with no contact was carried out, and the coated support was dried with an air of the dry-bulb of 23°C to 45°C and the wet-bulb of 15°C to 21°C in a helical type contactless drying apparatus.

After drying, moisture conditioning was performed at 25°C in the humidity of 40% RH to 60% RH. Then, the film surface was heated to be 70°C to

90°C. After heating, the film surface was cooled to 25°C.

[0431]

Thus prepared photothermographic material had the matness of 550 seconds on the image forming layer side surface, and 130 seconds on the back surface as Beck's smoothness. In addition, measurement of the pH of the film surface on the image forming layer side surface gave the result of 6.0.

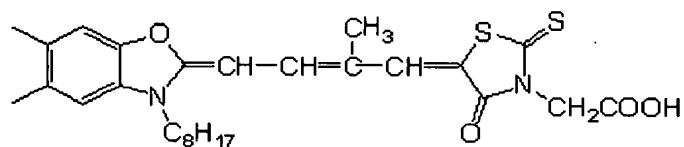
[0432]

Chemical structures of the compounds used in Examples of the invention are shown below.

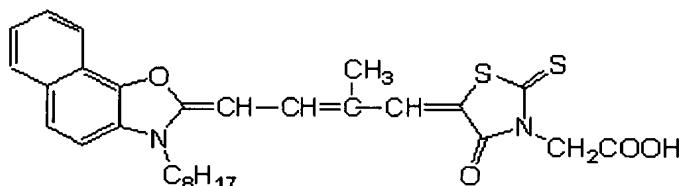
[0433]

[Formula 30]

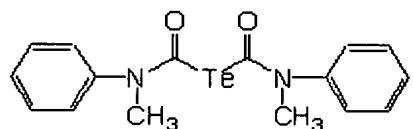
Spectral Sensitizing Dye A



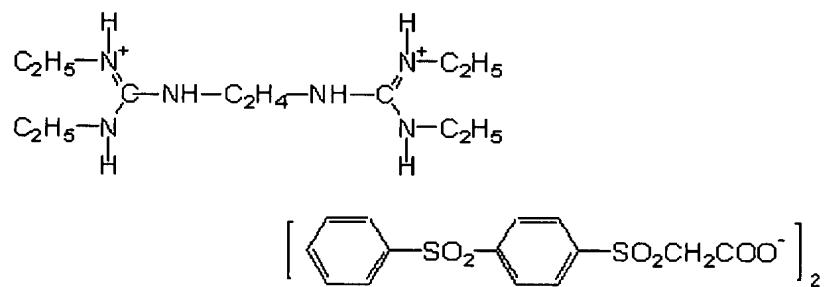
Spectral Sensitizing Dye B



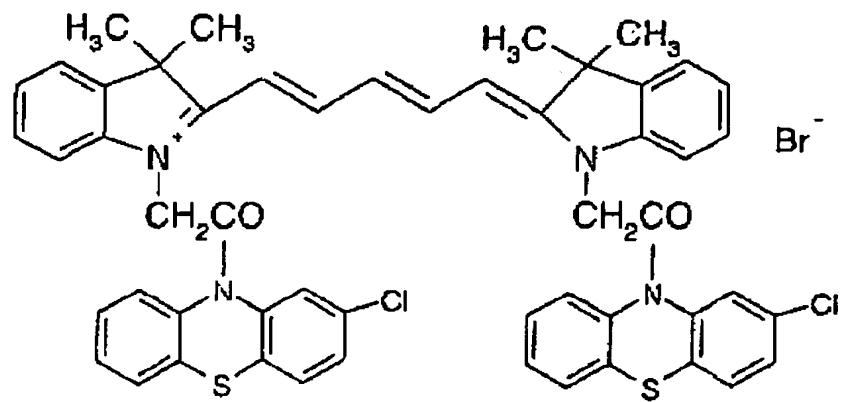
Tellurium Sensitizer C



Base Precursor Compound-1



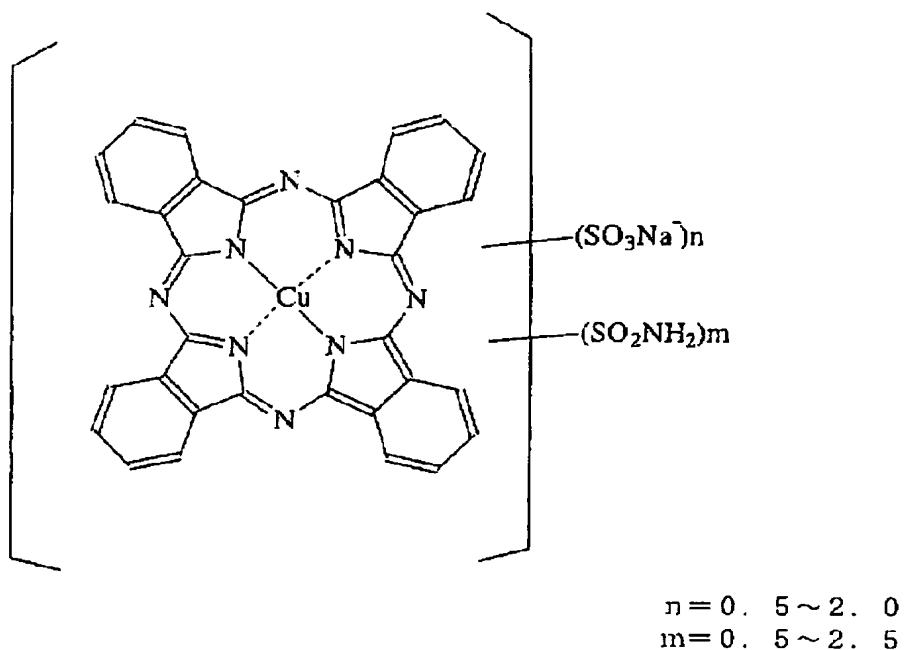
Cyanine Dye Compound-1



[0434]

[Formula 31]

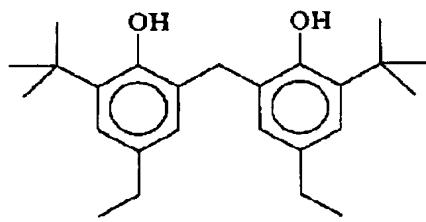
Blue Dye Compound-1



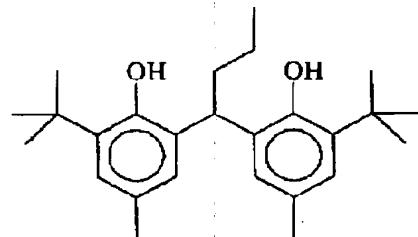
[0435]

[Formula 32]

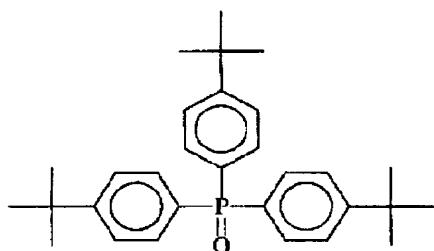
(Reducing agent 1)



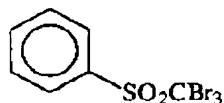
(Reducing agent 2)



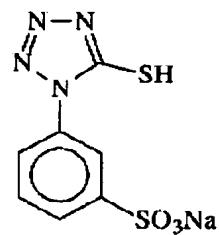
(Hydrogen bonding compound-1)



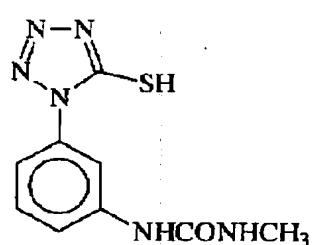
(Organic halogen compound-4)



(Mercapto compound-1)



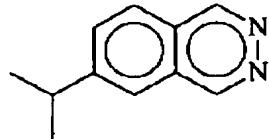
(Mercapto compound-2)



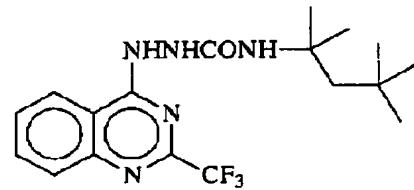
[0436]

[Formula 33]

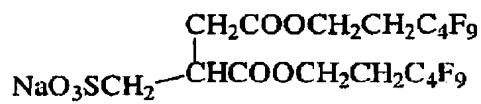
(Phthalazine compound-1)



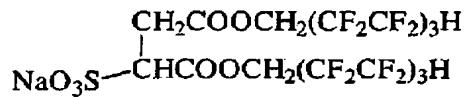
(Development accelerator-1)



(F - 1)



(F - 2)



[0437]

4. Evaluation of Photographic Properties

1) Preparation

The resulting sample was cut into a half-cut size (43 cm in length x 35 cm

in width), and was wrapped with the following packaging material under an environment of 25°C and 50% RH, and stored for 2 weeks at an ambient temperature. Therafter they were subjected to the following evaluations.

2) Packaging Material

PET 10 μm / PE 12 μm / aluminum foil 9 μm / Ny 15 μm / polyethylene 50 μm containing carbon at 3% by mass; oxygen permeability at 25°C: 0.02 $\text{mL}\cdot\text{atm}\cdot\text{m}^2\cdot\text{day}$; vapor permeability at 25°C: 0.10 $\text{g}\cdot\text{atm}\cdot\text{m}^2\cdot\text{day}$.

[0438]

3) Conditions of Exposure and Thermal Development of Photothermographic Materials

Exposure was performed on samples by a 660 nm laser diode using an image recording apparatus which has the structure shown in Fig.1. The distance between the laser irradiation part and the thermal development insertion part was set to be the distance shown in Table 1 by adjusting the length of the guide plate 32 and thermal development was performed.

Thermal development was performed in conditions that 3 panel heaters were set to be 112°C - 119°C - 121°C, and a total thermal development time was set to 14 seconds.

[0439]

4) Evaluation of Photographic Properties when Continuously Processing 20 Sheets

20 sheets of each of the photothermographic material 1 to 4 were continuously exposed and thermal developed by the condition described above,

and sensitivities of each of 1st, 5th, 10th and 20th sheets were shown in Table 1.

[0440]

Sensitivity (S) is defined as a reciprocal of an exposure value at which an optical density of $\text{fog}+1.0$ is obtained, and a sensitivity of the 1st sheet of the photothermographic material-1 is set to 100 and relative sensitivities were shown. A larger relative sensitivity value means a higher sensitivity.

[0441]

As apparent from Table 1, according to photothermographic material-4, when the distance between the laser exposing portion and the thermal developing portion becomes short, sensitivity becomes low together with increasing the number of continuously processed sheets. In order to obtain a stable sensitivity, the distance has to be 75 cm or more, and preferably 100 cm or more, and therefore the plan for reducing the size of the apparatus is difficult. On the contrary hand, as for photothermographic material-1 to -3, even though this distance was set to be 45 cm, sensitivity varies within 1%, and gave extremely excellent results.

[0442]

[Table 1]

Test No.	Photothermographic Material	Organic Polyhalogen Compound	Path Length (cm)*	Sensitivity (S)				Remarks
				1st Sheet	5th Sheet	10th Sheet	15th Sheet	
1	Photothermographic Material-1	Organic Polyhalogen Compound-1 (1a-1)	40	100	99	98	98	Present Invention
2	Photothermographic Material-1	Organic Polyhalogen Compound-1 (1a-1)	45	100	100	99	99	Present Invention
3	Photothermographic Material-1	Organic Polyhalogen Compound-1 (1a-1)	55	100	100	100	100	Comparative Example
4	Photothermographic Material-1	Organic Polyhalogen Compound-1 (1a-1)	75	100	100	100	100	Comparative Example
5	Photothermographic Material-1	Organic Polyhalogen Compound-1 (1a-1)	100	100	100	100	100	Comparative Example
6	Photothermographic Material-2	Organic Polyhalogen Compound-2 (1b-30)	40	102	102	101	101	Present Invention
7	Photothermographic Material-2	Organic Polyhalogen Compound-2 (1b-30)	45	102	102	102	101	Present Invention
8	Photothermographic Material-2	Organic Polyhalogen Compound-2 (1b-30)	55	102	102	102	102	Comparative Example
9	Photothermographic Material-2	Organic Polyhalogen Compound-2 (1b-30)	75	102	102	102	102	Comparative Example
10	Photothermographic Material-2	Organic Polyhalogen Compound-2 (1b-30)	100	102	102	102	102	Comparative Example
11.	Photothermographic Material-3	Organic Polyhalogen Compound-2 (1c-1)	40	101	99	99	99	Present Invention
12	Photothermographic Material-3	Organic Polyhalogen Compound-2 (1c-1)	45	101	101	100	100	Present Invention
13	Photothermographic Material-3	Organic Polyhalogen Compound-2 (1c-1)	55	101	101	101	101	Comparative Example
14	Photothermographic Material-3	Organic Polyhalogen Compound-2 (1c-1)	75	101	101	101	101	Comparative Example
15	Photothermographic Material-3	Organic Polyhalogen Compound-2 (1c-1)	100	101	101	101	101	Comparative Example
16	Photothermographic Material-4	Organic Polyhalogen Compound-4 (tribromomethane sulfonylbenzene)	40	100	97	90	80	Comparative Example
17	Photothermographic Material-4	Organic Polyhalogen Compound-4 (tribromomethane sulfonylbenzene)	45	100	99	93	85	75
18	Photothermographic Material-4	Organic Polyhalogen Compound-4 (tribromomethane sulfonylbenzene)	55	100	99	96	90	83
19	Photothermographic Material-4	Organic Polyhalogen Compound-4 (tribromomethane sulfonylbenzene)	75	100	100	99	99	Comparative Example
20	Photothermographic Material-4	Organic Polyhalogen Compound-4 (tribromomethane sulfonylbenzene)	100	100	100	100	100	Comparative Example

Note) *Path length: the length from the scanning line of the laser irradiation means to the insertion part of the thermal developing portion (cm)

[0607]

[Effects of the Invention]

According to the invention, an image forming method is provided that is capable of outputting an image with higher stability through laser exposure and thermal development of a photothermographic material using a compact apparatus.

[Brief Description of the Drawing]

[FIG. 1]

Fig. 1 is an image recording apparatus of the invention.

[Description of Reference Numerals]

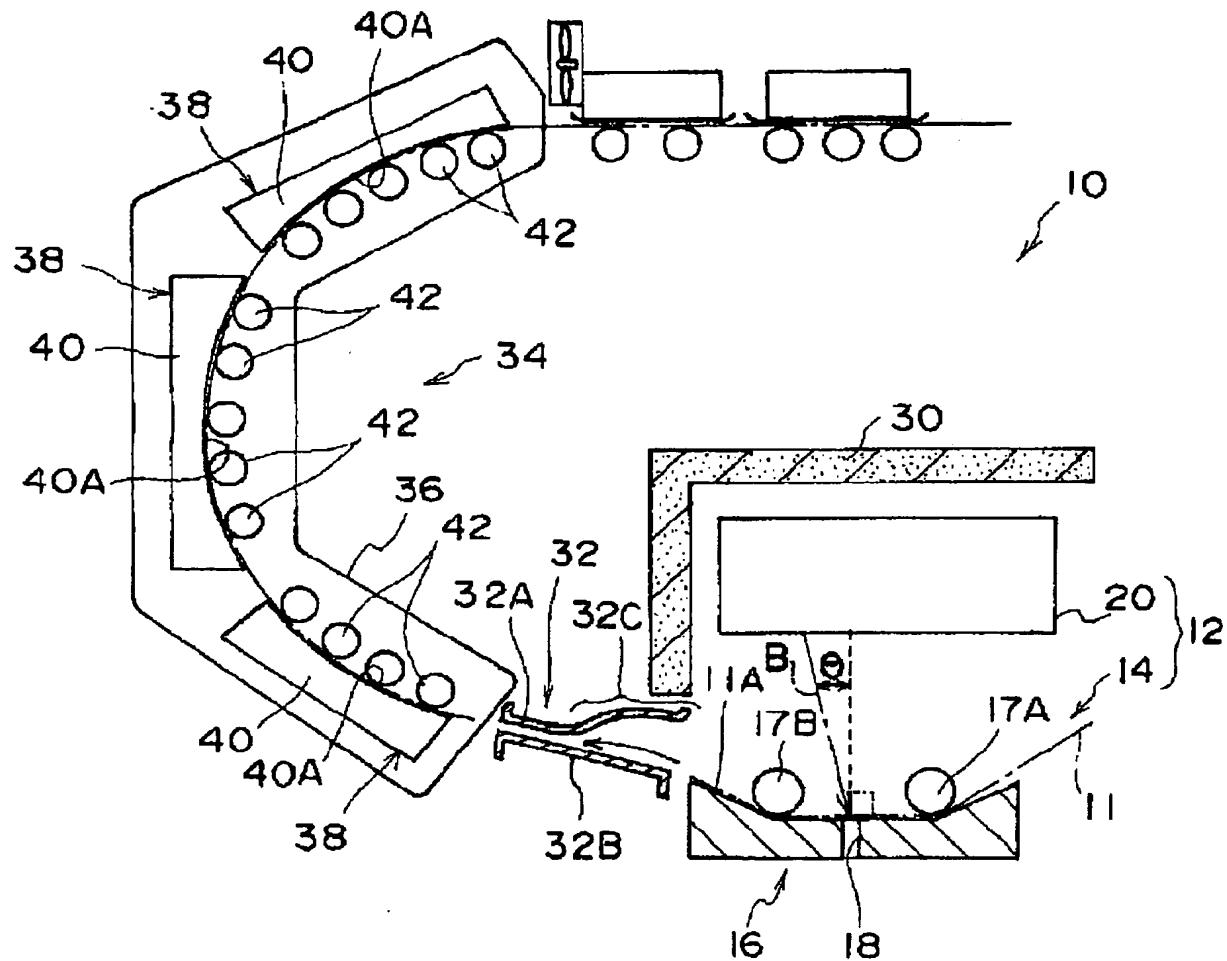
- 10 image recording apparatus
- 11 photothermographic material
- 11A recording surface of photothermographic material
- 12 exposing portion
- B laser beam
- 14 transport portion
- 16 press plate
- 17A, 17B driving rollers
- 18 through groove
- 20 scanning portion (laser irradiation means)
- 32 guide plate
- 32A top guide plate

- 32B bottom guide plate
- 32C expanding portion
- 34 thermal developing portion
- 36 casing
- 38 development unit
- 40 heating plate
- 40A heating surface
- 42 press roller

[DOCUMENT NAME]

DRAWING

[FIG. 1]



[DOCUMENT NAME]

ABSTRACT

[SUMMARY]

[OBJECT]

To provide an image forming method using a photothermographic material, capable of outputting an image with stable sensitivity, utilizing a compact apparatus for laser exposure and thermal development in which a laser exposing portion and a thermal developing portion are positioned close to each other.

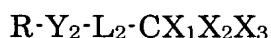
[MEANS FOR SOLUTION]

An image forming method for forming an image with an image recording apparatus including laser irradiation means for scan exposing, with a laser beam, a photothermographic material comprising a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder on at least one surface of a support, and means for transporting the photothermographic material in a sub scanning direction and guiding it to a thermal developing portion, wherein the photothermographic material comprises at least one compound selected from formulae (1a), (1b) and (1c), and a distance between a scanning line of the laser irradiation means and an insertion part of the thermal developing portion is 50 cm or less.

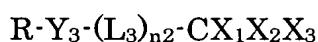
Formula (1a)



Formula (1b)



Formula (1c)



[SELECTED FIGURE]

None